Non – Catalytic Partial Oxidation of Sour Natural Gas

by

Tarique Hakeem

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

June, 1997

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ABSTRACT

The combustion of sour natural gas in oxygen under non catalytic partial oxidation conditions (NCPO) is investigated theoretically using simulation techniques. This involves the conversion of sulfur compounds represented by hydrogen sulfide gas into sulfur dioxide, along with the production of synthesis gas (H_2 and CO).

Separation of SO_2 gas from the synthesis gas is carried out by absorption in water to produce sulfurous acid which is the feed stock to what is known as "Modified Westinghouse Cycle", producing sulfuric acid and additional hydrogen.

A number of parameters were studied over the range indicated for the NCPO process as follows: Feed temperature from 900 ^{0}F and 1200 ^{0}F, equivalence ratio from 0 to 1, H_2S content of gas feed from 0, 3, 5, 7 and 10% and composition of natural gas (ethane 5% and propane 5%).

The simulation was carried out using both AspenPlus and mathematical modeling. A two stage reaction mechanism is proposed which involves the complete combustion of some of the methane (along with H_2S), in the first stage followed by the second step in which surplus methane reacts with the primary reaction products to form the synthesis gas.

The role of various operating parameters in establishing the optimum yield of H_2 / CO gas mixture is presented and thoroughly discussed. An optimum conversion is achieved at an equilibrium ratio of about one-half, a pressure of 15 psi, feed temperature of 1200 ^{0}F, at a combustion chamber temperature of 2200 ^{0}F.

الملخص

احتراق الغاز الطبيعي الحامضي في الأكسجين تحت ظروف الأكسدة الغير محفزة (NCPO) المحققة نظرياً باستخدام الكمبيوتر وتحقيقاته التي تحتوي على تحويل مركبات الكبريت الممثلة بغاز كبرتيد الهيدروجين (H_2S) في ثاني أوكسيد الكبريت (SO_2) ، من خلال انتاج الغاز الاصطناعي ($CO + H_2$) .

فصل غاز ثاني اكسيد الكبريت (SO_2) من الغاز الاصطناعي يتم باقتصاصه لانتاج الحامض الكبريتي الذي يمثل المغذي الخام لما يعرف بـ (دارة وستنفهوس المعدلة) ، لانتاج الحامض الكبريتي وهيدروجين إضافي .

عدد من الثوابت المدروسة في النطاق المحدد لعملية الأكسدة الغير محفزة (NCPO) كما يلي : حرارة المورد المغذي للعملية تكون (٩٠٠ - ١٢٠٠) فهرنهايت ويحوي الغاز المغذي على نسبة صفر ، ١ ، ٣ ، ٥ ، ٧ ، ١٠٪ الهيدروجين (H_2S) وتركيز الغاز الطبيعي يكون ٥٪ إيتان و ٥٪ بروبان .

تحقيقات الكمبيوتر التي أنجزت باستخدام اسبن بلس (Aspen Plus) والنموذج الرياضي (الحسابية) تقنية التفاعل ذي المرحلتين اقترح لبحوث على الاحتراق الكامل لبعض الميثان مع كبريتد الهيدروجين (H_2S) في المرحلة الأولى الملحقة بالخطوة الثانية التي يتفاعل فيها الميثان الفائض مع نواتج التفاعل الأساسي لتكوين الغاز الاصطناعي .

دور ثوابت التشغيل السابقة هو لتثبيت درجة انتاج لمزيج غاز الهيدروجين (H_2) وأول أكسيد الكربون (CO) . وللحصول على درجة ملائمة في نسبة متعادلة تكون ١/٢ تقريباً ، وضغط ١٥ باوندا (لبره) انش ٢ (PSI) ، ودرجة حرارة المغذي تكون ١٢٠٠ فهرنهانيت ، ودرجة حرارة الاحتراق تكون ٢٢٠٠ فهرنهايت .

NOMENCLATURE

$\Delta G_{f_i}^{\circ}$	Standard Gibbs free energy of formation [Kcal/mol]
ΔG_R°	Standard Gibbs free energy of reaction [Kcal/mol]
H_i°	Standard enthalpy of individual components [Kcal/mol]
ΔH	Enthalpy of a compound [Kcal/mol]
ΔH_f°	Enthalpy of formation [Kcal/mol]
$\left(H^{\circ} - H_{298}^{\circ}\right)_T$	Heat content at temperature T ^{0}K [Kcal/mol]
ΔH_R°	Standard enthalpy of reaction [Kcal/mol]
H_{SO_2}	Henry's constant for SO_2 in water [atm]
H	Apparent Henry's constant for SO_2 in water [atm]
K	Equilibrium constant for the reaction 3.9 [atm]
K_1	Equilibrium constant for the reaction 3.7 [atm^{-1}]
K_P	Equilibrium constant [-]
K_2	Equilibrium constant for the reaction 3.3 [atm^2]
K_3	Equilibrium constant for the reaction 3.4 [atm^2]
K_4	Equilibrium constant for the reaction 3.5 [-]
P^*	Partial pressure of SO_2 [atm]
P	Total pressure [atm]
R	Universal gas constant [Kcal/mol]

T	Temperature [K]
T_P	Preheat temperature [K]
T_R	Combustion chamber temperature [K]
x_1	Mole fraction of methane in products
x_2	Mole fraction of carbon dioxide in products
x_3	Mole fraction of steam in products
x_4	Mole fraction of carbon monoxide in products
x_5	Mole fraction of hydrogen in products
x_6	Mole fraction of sulfur dioxide in products
x_7	Mole fraction of oxygen in feed per mole of methane in feed
x_8	Mole fraction of hydrogen sulfide in feed per mole of methane in feed
x_9	Total moles of product per mole of methane in feed
x_{SO_2}	Solubility of SO_2 in water [mole fraction]

Greek

α	Total concentration of SO_2 in the water [mol/mol]
ν_i	Stoichiometric coefficients

Subscripts

f	Formation
i	Number
R	Reaction
P	Preheat

CHAPTER 1

INTRODUCTION

Currently, synthesis gas is manufactured from various feedstocks such as natural gas, naptha, heavy oil, fuel oil, and coal. Natural gas is a naturally occurring combustible mixture of hydrocarbon and non-hydrocarbon gases found in porous formations beneath the earth's surface, often in association with crude petroleum. This is called associated gas. Being a gas it may occur alone in a reservoir. This is called free gas. Associated gas forms a cap between petroleum reservoir and the crude petroleum. Under high pressure, it is mixed or dissolved in crude petroleum.

Large reserves of natural gas are present in many oil producing countries. Much of this natural gas is sour (i.e., it contains varying amounts of H_2S gas) as shown in the Table 1.1. Natural gas is used as feedstock for the manufacture of synthesis gas. All the present processes for production of synthesis gas are catalytic. H_2S acts as a poison to the catalysts used in these processes. Hence, H_2S should be

removed before utilization of natural gas as a feedstock. Its concentration in the natural gas should be reduced to a level which prevents the poisoning of the catalyst.

Currently, synthesis gas is manufactured by steam reforming of sweet natural gas. This is a catalytic process in which the feed gas has to be sulfur free to avoid catalyst poisoning, As a result, acidic gas removal is a pre-requisite for the steam reforming process. H_2S is separated from the natural gas by one of the physiochemical separation methods. The separation process is expensive and involves the use of amine solvents. The chemisorption of acidic gas into the solvents is followed by regeneration of these solvents. Although the bulk production of synthesis gas is done via catalyzed steam reforming of sweet natural gas, uncatalyzed partial oxidation of sour natural gas with appropriate conditions may prove to be more attractive.

The main theme of the proposed work is to propose a novel scheme for manufacture of synthesis gas by partial oxidation of sour natural gas in the absence of catalysts. The partial combustion of sour natural gas with oxygen is examined with the following main objectives:

1. To propose a novel scheme for manufacture of synthesis gas by non-catalytic partial oxidation of sour natural gas.
2. To identify and classify the main chemical reactions taking place in the non

catalytic partial oxidation of sour natural gas in presence of oxygen.

3. To compile the basic thermodynamic data, physical constants such as, Gibbs free energy of the reactions, enthalpy of the reactions, equilibrium constants and typical operating ranges of the reactions involved as well as data on composition of natural gas produced in Saudi Arabia.
4. To simulate the non catalytic partial oxidation of the sour natural gas on Aspenplus. In this work, the simulation was carried out to study the effects of the following parameters :
    - Preheat temperature
    - Pressure
    - Equivalence ratio (O_2/CH_4)
    - H_2S composition in sour natural gas feed
    - Hydrocarbons heavier than CH_4 in sour natural gas feed
5. To compare the results of simulation with the actual data for a petrochemical plant in Saudi Arabia.

The proposed work is very relevant to Saudi Arabia. Saudi Arabia has large reserves of natural gas, which are used as feed to many industries. But, almost all of the natural gas produced in Saudi Arabia contains H_2S as shown in the Table 1.1. So, expensive processes are used to desulfurize it before utilization. The novel scheme proposed in this work does not require the desulfurization and provides additional by-products.

Table 1.1 Composition of gas produced in some fields in Saudi Arabia [Abdel-aal and Shalabi, 1996]

#	Field	Mole Percentage							
		N_2	CO_2	**H_2S**	C_1	C_2	C_3	C_4	C_{5+}
1	Ain Dar	0.3	11.85	**3.72**	45.87	19	11.66	4.5	3.09
2	Uthmaniyah	0.28	10.28	**1.78**	49.82	18.8	11.65	4.6	2.78
3	Fazran	0.11	7.45	**1.8**	54.71	19.9	10.51	3.65	1.84
4	Shedgum	1.23	9.88	**2.45**	49.37	18.2	11.28	4.51	3.13
5	Abqaiq	0.6	9.36	**3.23**	60.6	16.4	6.95	2.04	0.8
6	Abu Hadriyah	0.6	4.07	**5.12**	38.34	17.8	15.6	9.37	9.08
7	Berri	0.24	7.97	**7.74**	52.9	19.2	8.44	2.45	1.06
8	Khurais	0.5	5.25	**0.23**	41.91	23.7	17.85	6.73	3.79
9	Manifah	-	11.43	**16.05**	28.21	18.6	16.61	6.09	3.11
10	Marjan	0.32	1.47	-	80.48	10.9	4.5	1.58	0.73
11	Haradh	0.39	9.43	**1.17**	55.87	18.32	10.01	3.23	1.58
12	Hawiyah	-	10.90	**1.30**	56.70	17.40	9.20	3.0	1.50
13	Abu Safah	3.52	6.82	**2.90**	48.90	19.30	12.21	4.54	1.81
14	Damman	11.99	10.06	**1.66**	69.46	3.01	1.51	1.08	1.23
15	Haramliyah	0.08	9.38	**6.23**	47.62	19.48	10.72	4.00	2.49
16	Khursaniyah	0.27	6.39	**3.77**	41.62	20.38	15.99	6.99	4.59
17	Qatif	0.39	17.50	**14.10**	34.44	15.50	11.64	4.24	2.16
18	Safaniyah	1.49	1.87	-	48.79	23.35	11.40	8.80	4.30
19	Zuluf	0.48	1.07	-	77.57	12.03	5.58	1.10	0.91

CHAPTER 2

LITERATURE REVIEW

Synthesis gas is the mixture of H_2 and CO used as a feedstock for petrochemical plants. The typical composition of synthesis gas for different processes is presented in the Table 2.1. Synthesis gas manufacture technology is well established. The common feed stocks are natural gas, naphtha, coal, heavy fuel oil, residual oil, water etc.. The most common conventional processes are

- Partial oxidation of residual oil
- Steam reforming of natural gas
- Gasification of coal
- Steam-iron process
- Water electrolysis

The advanced processes for manufacture of synthesis gas are

- High temperature electrolysis of steam

Table 2.1 Composition of synthesis gas depending on the end use

Synthesis Gas	**Main Uses**
$3H_2$:$1N_2$	Ammonia
$2H_2$:1CO	Methanol
$1H_2$:1CO	Oxo reaction
Pure CO, or CO + H_2O	Phosgene; formic, oxalic, acetic, glycolic, propionic and neo-acids; acrylates
Pure H_2	Hydrogen peroxide, various reduction and hydrogenation processes

- Integrated coal gasification and high temperature electrolysis
- Thermal cracking of natural gas
- HYDROCARB thermal conversion of coal
- Solar photo-voltaic water electrolysis
- By-product hydrogen from chemical industry
- Partial oxidation of methane in solid fuel cell

The advanced processes for the manufacture of synthesis gas are in the experimental stage. These have not been utilized industrially. The most common processes used worldwide for production of synthesis gas are

- Steam reforming of natural gas
- Steam reforming of naphtha
- Partial oxidation of fuel oil
- Partial oxidation of naphtha.

The literature on the production of synthesis gas using natural gas as a feedstock has been reviewed thoroughly. The review is divided into three categories :

- Steam Reforming
- Catalytic Partial Oxidation (CPO)
- Non-catalytic Partial Oxidation (NCPO)

The literature review of the most significant contributions in the field of synthesis gas production from natural gas has been summarized in the Table 2.2.

Table 2.2. Summary of the literature review in the field of the synthesis gas production from natural gas

Year	Investigator	Comments
1951	Mungen, R. and Kratzer, M. B.,	Partial combustion of sweet methane with oxygen • Experimental investigation
1971	Karim, G. A. and D' Souza, M. V.	Analytical examination of combustion of gaseous fuels • Proposed 25 step mechanism for sweet methane combustion
1974	Strelzoff, Samuel	Comparative study of the industrial partial oxidation processes of Shell and Texaco • Fuel Oil as feedstock • Process characteristics • Operational problems • Economics
1980	Reed, C. L. and Kuhre, C. J.	Studied the various aspects of the SHELL Gasification Process (SGP)
1984	Warnatz, J.	Studied the chemistry of high temperature combustion of alkanes up to octane
1985	Gesser, H. D. et al..	Studied partial oxidation of methane • Experimental • Catalytic • Methanol (yield up to 30-40%)
1986	Hanna, M. and Karim, G. A.	Studied combustion of lean mixtures of gaseous fuels • Equivalence ratio from 0.2 to 1.6 • Proposed 38 step mechanism for sweet methane combustion
1990	Mackie, J. C. and Hart, M. G.	Studied partial oxidation of sweet methane by N_2O
1991	Helton, T. E.	Studied the partial oxidation of sweet methane • Experimental • Catalytic (V_2O_5, MoO_2 etc.) • Methanol
1992	Karim, G. A. and Hanafi, A. S.	Studied the rich mixture of sweet methane and oxygen • Analytical • Temperature range 800-2000 K • Proposed 108 step mechanism

1992	Foral, M. J.	Studied the catalytic partial oxidation of sweet natural gas • Experimental • Catalytic (Quartz lined reactor) • Methanol
1993	Karim, G. A. and Zhou, G.	Studied the combustion of sweet natural gas with air
1993	Chun Jin-Woo and Anthony, R. G.	Studied partial oxidation of sweet methane • Experimental • Catalytic • Methanol (yield 34-55%)
1994	Jess A. and Hedden K.	Studied the production of synthesis gas by partial oxidation of methane with air and steam • Experimental • Catalytic • Temperature 1400 C
1994	Arutyanov V. S. et al.	Studied influence of pressure on the formation of products of partial oxidation of sweet methane • Experimental • Catalytic • Low temperature 400 C • High pressure 100 atm. • Methanol
1995	Arutyanov V. S. et al.	Studied influence of H_2, CO, N_2, on partial oxidation of sweet methane • Experimental • Catalytic • Low temperature 400 C • High pressure 100 atm. • Methanol (yield 30-50%)
1995	Dave N. and Foulds G. A.	Compared catalytic partial oxidation process and steam-reforming for production of methanol from natural gas • ASPEN • Catalytic • Economics
1996	Abdel Aal, H. K. and Shalabi M. A.	Proposed the partial oxidation process from sour natural gas • Non catalytic • Synthesis gas manufacture • No desulfurization required • No external heating required

2.1 Steam Reforming

Steam reforming of natural gas is more economical than steam reforming of naphtha [SRI,1978]. But, the latter is used in areas where natural gas is scarce or expensive coupled with abundant supply of naphtha. Steam reforming is a catalytic process which is the most economical and the most widely used process for synthesis gas manufacture from natural gas. The catalyst used in steam reforming is sensitive to sulfur impurities and carbon deposition. Reforming is highly endothermic and the method of delivering the requisite heat to the immediate reaction area constitutes one of the biggest problems of the process.

Reactions of steam and hydrocarbons are not as rapid as those of oxygen and hydrocarbons [Vorum, 1969]. Catalysts are used to attain rates of commercial interest. Since the reaction is endothermic, higher rate of reaction needs a larger amount of heat. The feed ranges from methane to petroleum naphtha. The problems of operation increase with molecular weight of the feedstock, in terms of the amount of steam which must be mixed with the hydrocarbon and likelihood of carbon formation. The hydrocarbon should be virtually free from sulfur and its compounds, to prevent poisoning of the catalyst. Presence of sulfur and its compounds increases the probability of corrosion at such high temperature of operations.

Another desirable feature in feed is a high degree of saturation of the hydrocarbon

molecules [SRI, 1978]. Unsaturated feed molecules are relatively prone to cracking and carbon deposition, which results in lower activity of the catalyst. In the steam reforming process Ni-Cr catalyst is used for its activity and longevity. The required sulfur concentration should be less than 0.5 ppm. At excessively high temperature carbon is deposited which reduces the activity of the catalyst.

About 87% of the world synthesis gas is manufactured by steam reforming [SRI, 1978]. The partial oxidation share is 10%. Naphtha boiling below 220 ^{0}C is used for steam reforming because naphtha boiling above 220 ^{0}C forms carbon deposits.

After steam reforming, the acid gases of CO_2 and CO are removed from the synthesis gas [Dave and Foulds, 1995]. Then, the gas stream is shifted to adjust the H_2/CO ratio required for a particular process. Synthesis gas is supplied for production of a wide variety of petrochemical products such as urea and methanol. This is called two-step process application.

Apart from its use in the production of the petrochemicals, hydrogen is used in hydrotreating, hydrodesulfurisation and hydrocracking processes, while hydrogen and carbon monoxide are used as reducing agents in the steel industry [Dave and Foulds, 1995].

The thermodynamics of synthesis gas production by reacting light hydrocarbons with

steam and carbon dioxide has been studied [Reitmeier et al.., 1948]. The operating conditions of temperature, pressure and oxygen to methane ratio for maximum yield of synthesis gas per mole of oxygen and per mole of methane has been determined. Isothermal operation was assumed. The problem of carbon deposition was observed at equilibrium conditions and when gases were cooled. The process under consideration was carried out by reacting a mixture of hydrocarbon and steam over a catalytic material in a furnace at high temperature to form a mixture of hydrogen, carbon monoxide and carbon dioxide. *This was the earliest conception of steam reforming process.*

The operating conditions were determined to produce a wide range of composition of synthesis gas without deposition of carbon on the catalyst. Deposition of carbon can be further prevented by proper selection of equipment and operating conditions. Laboratory experimental work for steam reforming [Reitmeier et al.., 1948] was carried out to determine whether the results of thermodynamic calculations could be validated by experiment. Nickel catalyst was chosen for its high activity in promoting reactions between light hydrocarbons and steam and little activity for side reactions resulting in carbon formation. The theoretical calculations were validated by the experiment. Further, pilot plant studies were carried out under similar conditions and equipment. The capacity of the pilot plant was 6000 cu.ft./day. Pilot plant results were similar to the experimental results. Pilot plant study and experimental results clearly indicated the steam reforming process is feasible on industrial scale and synthesis gas could be produced from light hydrocarbons and steam at practical plant capacities and temperature without

encountering difficulties through the deposition of carbon.

Thermodynamic calculations for steam reforming were carried out to prepare a chart for determining an equilibrium mixture, outside the carbon deposition boundary [Reitmeier et al.., 1948]. Consumption of steam and carbon monoxide depends on the excess oxygen required to prevent carbon deposition at equilibrium. It was assumed that only carbon monoxide and hydrogen are formed, with no carbon, acetylene or ethylene formed. The maximum yield of H_2 and the minimum consumption of carbon dioxide and steam are favored by high temperature and low pressures. It was concluded that a catalyst is necessary for maximum yields in the steam reforming process.

The first commercial scale plant of steam reforming used industrial size equipment to produce synthesis gas of suitable purity and suitable hydrogen to carbon monoxide ratios for Fischer-Tropsch synthesis [Clarke et al., 1949]. A wide range of synthesis gas compositions can be produced on a commercial scale and hydrogen to carbon monoxide ratio can be controlled as required. Reaction of methane with water and CO_2 are both highly endothermic, so natural gas or low grade oil is burnt in a furnace and the gas is used to supply the heat in the reformer. The gas is later passed through a waste heat boiler to generate steam. Cooled products are scrubbed with amine solution to recover CO_2 needed as process material. It was observed that effluent gas used for heating the reformer has low CO_2 content (2%). Such a gas would be suitable for the production of synthetic fuels or chemicals without the removal of CO_2 . This process has low operating as well as low

capital costs since no CO_2 removal will be required for purifying the synthesis gas. Utility requirements for the production of synthesis gas would also be reduced as a result of the reduction of the steam requirements. Some modification in the plant equipment will be required to enable the production of such a synthesis gas low in CO_2 without the formation of carbon on the catalyst, but the modification will result in no appreciable increase in the cost of the plant and the simplicity of operation will remain essentially unchanged.

To obtain high carbon monoxide to hydrogen ratios required in many of synthesis gas mixtures, it is necessary to introduce carbon dioxide into reformer furnace to replace part or all of the steam used to react with the hydrocarbon [Dotterweich, 1969]. For medium carbon monoxide to hydrogen ratios, comparable amounts of carbon dioxide and steam should be introduced in reformer. For low carbon monoxide to hydrogen ratio, low amounts of carbon dioxide and large amount of steam should be introduced in the reformer

Reforming is a highly endothermic process. The method of delivering the requisite heat to the reaction area is the biggest problem in conducting the process, but it also provides the basis for classifying the various systems - externally heated continuous and internally heated and either continuous or cyclic.

Reactions of steam and hydrocarbons are by no means as rapid as those of oxygen and

hydrocarbons [Wellman and katell, 1963]. Use of catalysts is necessary to obtain substantial reaction rates. The externally heated and continuous type furnace is better than the internally heated one.

In the case of the methane-steam reaction, the application of pressure is disadvantageous to the reaction equilibrium [Wellman and katell, 1963]. This effect of increasing pressure of the equilibrium can be partly offset by raising the temperature. If air is used in methane oxygen process, the products are contaminated with nitrogen, which is disadvantageous for most purposes, except for manufacture of ammonia. Use of the pure oxygen adds to the material costs of the process.

Synthesis gas is used in the production of the oxo-alcohol [Van den Berg et al., 1970]. Three routes to the synthesis gas for production of oxo-alcohol - natural gas reforming, light naphtha reforming, and partial oxidation of heavy fuel oil- were compared from the point of the view of process economics. The partial oxidation of the heavy fuel oil was found to be most economical process. This study was carried out in Europe, where the price of heavy oil is sufficiently cheaper than naphtha or natural gas.

The conventional way to use natural gas is the steam reforming process, where it is reacted with water using a nickel based catalyst, forming synthesis gas, a mixture of carbon monoxide, carbon dioxide and hydrogen [Hutchins and Joyner, 1994]. The synthesis gas can be converted into methanol, over a copper/zinc oxide/alumina catalyst,

or to a mixture of straight chain alkanes and alkenes, using Fischer-Tropsch chemistry.

Steam reforming is a reliable and established technology, but it involves a highly endothermic reaction and as a result in an energy intensive process [Dave and Foulds, 1995]. It requires a separate fuel stream and CO_2 import if synthesis gas stoichiometric number close to 2 is required. {SN= $(H_2 - CO_2)/(CO - CO_2)$ }. The net result is a large furnace chamber, with associated high plant capital costs which, together with concomitant metallurgical constraints, contribute to the unsuitability of conventional steam reforming for off-shore application. Direct catalytic partial oxidation of methane to methanol is proposed and compared to steam reforming. Both the processes are simulated over the state-of-the-art process flowsheeting simulator Aspenplus by considering the same base case. Oxygen is injected separately, since introducing a premixed feed with the desired O_2/CH_4 ratio of 0.5 is fraught with danger, particularly if no steam or little steam cofeed is used, as it is well within the explosion limit at the reaction temperatures being considered. Very rapid transfer of the gas mixtures to the catalytic zone is required if the possibility of flashback and the occurrence of gas-phase reactions are going to be minimized. The occurrence of hot spots in the combustion chamber should be avoided for the same reason. On the basis of net energy requirement, catalytic partial oxidation (CPO) is on par with the alternative synthesis gas technologies.

Steam reforming is the most common method for the bulk production of hydrogen. Very large quantities of the raw materials and equipment sizes are involved. The heat required

for the highly endothermic and relatively slow reforming reaction is supplied externally. To increase the reaction rate would require still higher rates of heat supply. To achieve higher rates at the low temperatures, the process is assisted by the use of catalysts. However, it does not require expensive feed components. It requires expensive, hard to maintain equipment to transfer the necessary heat to the reaction zone . If the feed stock contains the sulfur bearing impurities, then the feed should be desulfurized before the reforming, in order to avoid the poisoning of the reforming catalysts [Karim and Hanafi, 1992].

2.2 Catalytic Partial Oxidation

Since the beginning of this century, investigators have been studying the oxidation of methane. In 1932, Bone and Allum studied the slow combustion of the methane at 450 C and 600 atm in borosilicate glass tubes and isolated 20% formaldehyde, methyl alcohol and formic acid. In 1936, Bone and Gardner showed that slow combustion takes place in two stages. There is an initial *induction period*, when the reaction rate is small and change in reaction rate is also small. After this initial *induction period*, there is a sudden increase in the reaction rate and change in reaction rate is also very large. This behavior is characteristic of *chain reactions*. During the initial *induction period*, the radicals are formed in small numbers, then in the *post induction period*, these radicals attack the molecules and the oxidation proceeds as a flame [Semenov, 1939; 1959]. In 1936, Bone and Gardner showed that *induction period* in the slow combustion of methane varies with temperature, pressure, composition and surface/volume ratio. The *induction period* may

be lengthened by increasing the surface/volume ratio of the reaction vessel and it may be shortened by raising the temperature or increasing the pressure of the reacting medium.

In 1937, Boomer and Thomas studied the oxidation of a mixture of natural gas and air passed over copper and silver catalysts and effects of temperature, pressure, composition and space velocity. The temperature range was 350-500 ^{0}C and pressure range was 140-230 atm. Principal product was methanol. It was observed that sulfur poisoned the catalysts effectively. Copper catalyst provided metal surfaces that easily oxidized and reduced and helped in dissipation of the heat of reaction. Gas phase reactions were determined and lack of control of temperature was observed. Desired reactions take place on surfaces and are highly sensitive.

Catalytic partial oxidation of sweet methane has been studied [Latta and Walker, 1948]. The sweet natural gas and oxygen is passed over cheap iron catalyst [Latta and Walker, 1948] in a fluidized bed yielding hydrocarbons as principal products, with smaller amounts of oxygenated derivatives as byproducts. Synthetic hydrocarbons were recovered and by relatively simple refining process were converted to high quality gasoline and heavier liquid fuels. Oxygenated compounds were obtained in complex mixtures which were processed for separation of individual components.

The potential for direct catalytic partial oxidation of methane to methanol has been evaluated by Edwards and Foster in 1986. The direct catalytic process has the advantage

over the conventional process that it eliminates the need for steam reforming. The overall performance of steam reforming is limited by the high cost and inefficiencies associated with the process. Catalytic partial oxidation has the potential for reducing the cost of methanol provided the total oxidation of methane to CO_2 and water is minimized.

Natural gas mixtures with oxygen or air were passed over supported transition metal catalysts to obtain yields of synthesis gas over 90% [Vernon et al., 1992]. The catalytic partial oxidation of methane was carried out using carbon dioxide as the oxidant. The catalytic partial oxidation process has several advantages over steam reforming process. The catalytic partial oxidation has greater selectivity for synthesis gas production, is exothermal, and has more desirable CO/H_2 ratio of the product.

The partial oxidation of methane by oxygen giving synthesis gas can be catalyzed to thermodynamic equilibrium using the transition metals Ni, Ru, Rh, Pd, Pt and Ir supported on inert oxides [Hutchins and Joyner, 1991]. The yield of CO and H_2 increases with increase in temperature (650-1050 ^{0}K) and decreases with increasing pressure from 1 to 20 atm. The gas mixture N_2 : CH_4 : O_2 at the ratio 4 : 2 : 1 at 1050 ^{0}K and 1 atm with space velocity of $4 * 10^4$ $hour^{-1}$ gives an ~92% yield of synthesis gas. Under similar conditions of temperature and pressure, catalysts such as iridium on are active for the combined partial oxidation and carbon dioxide reforming reaction giving synthesis gas in similarly high yield.

During the direct partial oxidation of methane to formaldehyde over a 2% V_2O_5 / SiO_2 catalyst with molecular oxygen as oxidant, the surface residence times and concentrations of various intermediates showed that formaldehyde is the primary reaction product. As methane conversion increased, formaldehyde selectivity decreases rapidly while CO_x selectivity increased, indicating that formaldehyde was a primary product of the reaction, while CO_x formation occurred apparently in large part by secondary reaction [Koranne et al., 1993].

At selectivities higher than 77% the direct catalytic methane to methanol (DMTM) process is preferable in comparison to the conventional route via synthesis gas [Arutyanov et al., 1995; Edwards and Foster, 1986]. The gas phase process will be preferable at selectivities no higher than 70% due to the absence of catalyst and carbon dioxide removal. The DMTM process permits the construction of relatively simple modular factory-made installations with a desirable capacity from hundred tons to hundreds of thousand tons per year in remote areas near the place of consumption of these products thus removing transportation costs.

Pressure has significant effect on the yields of methanol below the pressure of 100 atm [Arutyanov et L., 1994]. But, pressure in excess of 100 atm has no profound effect on the process. Hydrogen present in the feed gas also affects the yield of methanol. The yield of methanol decreases if hydrogen concentration in the feed gas is in excess of 5%. It shows decreasing trend for CO concentrations below 15%. Presence of both hydrogen below 5%

and CO above 15% has no effect on the yield of the methanol.

Production of synthesis gas by catalytic partial oxidation of methane with air has been studied in a semi-technical adiabatic reactor [Jess and Hedden, 1994]. The molar ratio of oxygen to methane must be higher than 0.5 to avoid soot formation, especially at relative low temperatures. Catalytic partial oxidation of natural gas is a low cost process. The process has very short residence times. The ratio of H_2/CO can be increased by the addition of steam.

2.3 Non-Catalytic Partial Oxidation

Steam reforming reactions are endothermic, so external heat is supplied by burning the natural gas in a furnace. It was observed that effluent gas used for heating the reformer has low CO_2 content (2%) [Clark et al., 1949]. Such a gas would be suitable for the production of synthetic fuels or chemicals without the removal of CO_2. This process has operating as well as low capital costs since no CO_2 removal will be required for purifying the synthesis gas. Utility requirements for the production of synthesis gas would also be reduced as a result of the reduction of the steam requirements. Some modification in the plant equipment will be required to enable the production of such a synthesis gas low in CO_2, but the modification will result in no appreciable increase in the cost of the plant and simplicity of operation will remain essentially unchanged. *This was the earliest conception of the partial oxidation of the sweet methane.*

The thermodynamics of the synthesis gas production by partial oxidation of sweet methane has been studied by Mayland and Hayes in 1949. The conditions of temperature, pressure and oxygen to methane ratio for maximum yield of synthesis gas per mole of oxygen and per mole of methane has been determined. Isothermal operation was assumed. The problem of carbon deposition was observed at equilibrium conditions and when gases were cooled.

The partial oxidation of sweet methane with oxygen at 15 psi has been studied on pilot plant scale [Mungen & Kratzer, 1951]. The independent variables were the ratio of oxygen to carbon in the feed, the preheat temperatures of feed stream and the space velocity. The reaction is assumed to proceed in two steps – a primary reaction when carbon dioxide and water are the main products of the reactions of methane and oxygen, followed by reforming of methane with carbon dioxide and water to carbon monoxide and water. The combustion chamber temperature was varied from 2000 ^{0}F to 2500 ^{0}F. To ensure good feed conversion rates, high temperatures of order of 2200 ^{0}F are needed. The partial combustion of methane with oxygen under assumed commercial conditions was shown to be a practical method of supplying feed gas to the hydrocarbon synthesis process.

The pilot plant study continued with carrying it out for various feeds, i.e., sweet methane, fuel oil and coal tar [Eastman, 1956]. The results with sweet methane were obtained in a

generator of commercial size, whereas the results of the fuel oil and coal tar were obtained in a smaller pilot size generator. Further, these results were compared with calculated values from heat and material balances. The predicted oxygen consumption values were very close to observed values. The composition and temperature are critically dependent on the methane to oxygen ratio.

To improve the overall thermal efficiency of the process, preheating of the feedstock through heat exchange with the product gas is carried out and improving the combustion chamber insulation to produce higher operating temperatures since higher operating temperatures favors the endothermic reforming reaction [Karim and Hanafi, 1992]. In practical partial oxidation systems, the preheat temperature is limited. It was also found that pre-ignition did not occur up to a preheat temperature of 1700 ^{0}F and no oxidation products of methane were discovered up to a preheat temperature of 1200 ^{0}F but at 1700 ^{0}F, significant quantities were present. Some valuable C_2 -hydrocarbons were recovered for different temperature regions and residence times. An experimental study reported that acetylene was directly produced in the partial oxidation through a water quench within the residence time at the yield of up to 8.85% by dry volume.

The partial oxidation of methane with air to produce hydrogen for ammonia production is attractive, since part of the N_2 may be used to synthesize the product [Wellman and Katell, 1964]. Determining the product gas from the partial oxidation of methane requires the simultaneous solution of the equilibrium equations of the controlling reactions and a

thermal balance. The thermal balance is based on the oxygen to methane ratio, the heats of reactions and specific heats of the product gases. Partial oxidation is the combustion of methane with less than the required amount of oxygen needed for combustion.

The variation of the yields of the products of partial oxidation of sweet methane was investigated over a wide range of temperature, pressure and initial feed composition, on the assumption that thermodynamic chemical equilibrium is attained [Karim and Singh, 1967]. The result was presented in the form of charts, enabling the composition of the equilibrium products to be estimated, over a temperature range of 1700 ^{0}F to 2200 ^{0}F, a pressure range of 1 to 100 atmospheres and feed mixture strengths from just beyond the stoichiometric ratio to excessively rich mixtures up to the carbon formation boundary.

The overall kinetics of high temperature methane oxidation was studied in a flow combustion chamber [Nemeth and Sawyer, 1969]. Small quantity of reactants was injected at high velocity for rapid mixing through a quartz tube. Argon was used as the hot carrier gas. The overall rate expression was found out. The rate constant found experimentally was in reasonable agreement with the other reported values. The experimentally determined reaction orders were in good agreement with those reported in the flame studies and in the isothermal, low flow rate reactor. The activation energies reported are in good agreement with those reported in the shock tubes and well stirred reactor.

Partial oxidation of heavy oil was studied for operations at 30 atm. [Van den Berg et al.,

1966]. Operations at elevated pressures will result in lower compression costs. In the catalytic steam reforming of methane or naphtha the synthesis gas composition is essentially determined by equilibrium conditions so that any increase in operating pressure has to be accompanied by a compensating increase in operating temperature to keep the methane content of the synthesis gas below an acceptable limit. Partial oxidation of heavy fuel oil operates at such high temperatures that equilibrium contents of both carbon and methane are negligible. The actual presence of carbon and methane in measurable quantities in the synthesis gas is thus caused by the kinetic effects. An increase in operating pressure of the partial oxidation process therefore is not necessarily accompanied by an increase in carbon and methane content of the produced gas.

A study was carried out in Europe regarding the hydrogen manufacture [Van den Berg et al., 1971]. The economics of hydrogen production by partial oxidation of heavy residues at 55 and 90 atm [Shell] has been studied and compared with the catalytic steam reforming of light naphtha. It was found that when the price of naphtha exceeded the price of the residual fuel oil used in the partial oxidation process by more than $ 8.90/t for a 170t/day hydrogen plant and $10.0/t for a 100t/day plant, it was more economic to use the partial oxidation route. Also for an oil gasification process including a waste heat boiler, there was no incentive to increase the partial oxidation pressure above 55 atm because both the capital and operating costs increased.

The high temperature reaction of sweet methane in a flow system was investigated

analytically using a reaction scheme consisting of 24 reaction steps and involving 15 species [D'Souza and Karim, 1971]. Over the range of conditions considered the predicted yield of hydrogen and carbon monoxide compared favorably with the experimental evidence reported in the literature. The results also indicated the importance of hydrogen peroxide in the low temperature oxidation of methane particularly within the pre-ignition stage. Calculated values of the induction period were generally in good agreement with the experimental results reported in the literature.

The reaction of methane and oxygen was studied at atmospheric pressure and the temperature range 1100 K - 1400 K and equivalence ratios of 0.05 -0.5 [Dryer and Glassman, 1973]. Final oxidation products were carbon dioxide and water, and carbon monoxide was observed to be a major intermediate specie of increasing importance at lower reaction temperatures. The presence of two well defined stages (induction phase and post induction phase) was confirmed and the disappearance rate of methane was found to exhibit contrasting kinetic properties in these two stages. While the induction phase reaction was not quantitatively studied, the methane disappearance rate was qualitatively observed to be inhibited by the presence of methane and accelerated by the concentration of oxygen.

Existing processes of high pressure partial oxidation - Texaco , Shell and Union Carbide were compared [Strelzoff, 1974]. These processes were considered for different feeds. The first two were considered for naphtha, heavy fuel oil and residual oil and the third was

considered for coal. A novel scheme was presented for power generation with partial oxidation of naphtha, heavy oil and residual oil.

Synthesis gas can be produced by partial oxidation of a wide variety of fluid hydrocarbons using the Shell gasification process [Reed and Kuhre, 1979; Cox and Williamson, 1977]. Shell gasification process offers important advantages :

- It has broad flexibility in feedstocks, ranging from light hydrocarbons to asphalt. Operation can be easily switched to alternate feedstocks, depending on availability and minimum cost.
- The hydrogen to carbon monoxide ratio can be adjusted by proper selection of the feedstock, varying the addition of moderating steam or by recycling carbon dioxide to the combustion chamber.

Most common feedstocks for synthesis gas- namely natural gas, naphtha, fuel oil and coal were evaluated for investment, operating and manufacturing costs [Czuppon and Buividas, 1979]. The conclusions drawn with respect to the use of the various feedstocks were :

- The most economical feedstock was natural gas.
- If the cost of the natural gas approaches $ 3.50/MM Btu, other feedstock should be given serious consideration, including heavy oil and coal.
- Use of fuel oil and other heavy hydrocarbon feeds with the partial oxidation process would increase to a greater degree than previously, primarily because of the increasingly favorable price structure of these feeds.

- Greater emphasis will be placed on the use of lower grade fuels for firing both the reformer and auxiliary boilers in steam reformer units, either for flexibility or because of cost advantage.
- Coal based operations could be justified in locations where gas is not available and where the unit cost of coal is low, and the only alternative is expensive imported oil.

Principle units in the partial oxidation system for production of hydrogen include a gasifier section, a CO shift and a pressure swing adsorption (PSA) purification section [Abdel-aal and Shalabi, 1996]. If hydrogen is required as a product of steam reforming or partial oxidation process then pressure swing adsorption (PSA) is employed to obtain purity above 90% [Kirk and Othmer, 1980]. It is a single step process in which all the constituents, except hydrogen are simultaneously removed as the reformer effluent moves through the adsorbent bed. With a naphtha feed, the hydrogen from the PSA unit has a purity greater than 99.999 mol % with a CO content less than 10 ppm by volume and no carbon dioxide. If a feedstock containing nitrogen is used, the nitrogen can also removed to obtain the same purity.

Synthesis gas manufactured by any one of the processes is treated for removal acidic gases and then it is sent to another plant for production of various petrochemicals. This is called a two step process. However, both synthesis gas generation and petrochemical production can be carried out in a single direct process. This is called a one step process [Gesser et al., 1985]. Gesser et al., reviewed the direct conversion of methane to methanol process.

The conversion of methane to methanol is favored by high pressure, high temperature, and low oxygen concentration. The residence time, which primarily depended on the experimental system used, does not have a significant affect on methanol yield. Metal surfaces, such as nickel, copper, silver, steel, and certain alloys, have a catalytic effect The presence of higher alkanes, especially ethane has a favorable influence on the oxidation of methane to methanol.

In 1986, Tsang and Hampson produced a chemical kinetic database for combustion chemistry for methane and related compounds. This database consists of transport, thermodynamic and kinetic data for methane and compounds which are intermediate in the oxidation of methane.

In 1989, Brown et al. studied the homogeneous gas-phase partial oxidation instead of more popular catalytic partial oxidation. The successful conversion to methanol involves high pressure (10-50 atm.), moderate temperatures (550-750 ^{0}C) and low oxygen levels (2-10%). The reaction scheme developed for low temperature ignition was taken as the basis and supplemented with additional reactions relevant to these conditions.

In the process of direct process of non catalytic partial oxidation of natural gas to methanol the presence of higher hydrocarbons in the feed decreases the methane conversion and increases the total hydrocarbon conversion [Foral, 1992]. The lower oxygen concentrations improve methanol selectivity, but reduce per-mass methane

conversion. Methanol yield is maximized at oxygen concentrations above 8%. The optimum oxygen level will be a compromise between higher methanol yield (low oxygen concentrations) and higher per-pass methane conversions (higher oxygen concentrations).

Lower temperatures and higher pressures are desirable for maximizing both methanol yield and methane conversion. Average combustion chamber temperatures of 700-900 ^{0}F and a pressure of 1300 psig appear to be optimal within the ranges studied. Combustion chamber diameter (surface-to-volume ratio) can be an important parameter in this system. This is particularly true at low oxygen concentrations, where smaller diameter combustion chambers give the best results. In addition, packing the large diameter combustion chamber with quartz beads improves methanol selectivity at low oxygen concentrations (below 5 vol% O_2), but has little effect at higher oxygen levels.

The homogeneous partial oxidation of methane involves the primary reactions of methane oxidation as well as the secondary reactions with the reaction products formaldehyde, methanol, and carbon monoxide [Chun and Anthony, 1993]. The complex free-radical set of reactions were modeled using a pseudo-first-order reaction parallel-series network of the three reactions methane to methanol, methane to carbon monoxide, and methanol to carbon monoxide. The secondary reaction of methanol to carbon monoxide increases as the oxygen concentration in the feed increases. For experiments with 100% oxygen conversions, increases in residence time and temperature result in further loss of methane and methanol to CO. For temperatures greater than 710 ^{0}K some oxidative coupling

occurs to produce ethane. The selectivity of methanol was 34-55% for feeds of 2.3-4.4% oxygen and 95-98% methane and 50 atm. The selectivity was highest at low conversions and low oxygen feed concentrations.

Lean mixtures on combustion produce low final combustion temperatures [Hanna and Karim, 1986]. Higher combustion temperatures with lean mixtures are possible by preheating the mixture which requires supply of additional external heat. Increase in operating pressure tends to increase the final flame temperature. The concentrations of formaldehyde reach very high values in the early stages of the reaction that can be orders of magnitude greater than those eventually reached at the end of equilibrium conditions. The course of the oxidation reactions of methane should not be interrupted by quenching, to avoid such high concentrations of formaldehyde in reaction products.

Equivalence ratio is the ratio of number of moles of oxygen in the feed to the number of moles of methane in the feed. Improvement in the methane conversion and yield can be carried out by reducing the equivalence ratio and by pre-heating the reactants [Balthasar, 1984]. Extremely low hydrogen yields are obtained at low temperatures. At high temperatures, the time required to achieve the equilibrium concentrations is reduced. Very prompt quenching of the appropriate combustion zone at the appropriate time of the reaction may recover significant yields of C_2H_2 in the final products up to 10% by volume [Karim and Hanafi, 1989]. The hydrogen yield tends to be produced not only from the conversion of methane, but also through the subsequent consumption of some of the water

produced. Hence, sufficient time needs to be provided to produce hydrogen. Otherwise, the yield of hydrogen and ratio of hydrogen to carbon monoxide will both be low.

The maximum value of the reaction rate based on rate of disappearance of methane or oxygen in the fuel-rich mixture decreases almost linearly with equivalence ratio and takes longer to achieve. Longer reaction times should be provided as richer mixtures are employed. The methane disappearance rate is not directly related to the energy release rate or the temperature rise. Higher yields of hydrogen will be associated with constant volume conversion, in spite of the increase in combustion chamber pressure which would tend to reduce the hydrogen yield from equilibrium considerations. The production of higher temperatures under constant volume conditions comes about from the fact that the internal energy changes due to the energy release will be associated with a higher temperature rise than the corresponding enthalpy change under constant pressure combustion chamber operation [Karim and Zhou, 1993a].

A significant portion of the reaction time of rich methane-oxygen mixtures towards approaching the equilibrium state and producing the final products is usually taken up by the time needed to build up a host of active species such as radicals. The overall conversion processes will be speeded up by introducing active species in the initial feed. Similarly, increasing the concentration of diluents and/or other stable combustion products such as H_2S and CO_2 in the initial feed will tend to hinder the reaction processes and retard the overall conversion rate. Recirculation of combustion products to the feed stage

affects the progress of the oxidation reactions beneficially or adversely depending on the quantity of the gas being recirculated, its composition and mode of recirculation procedure. When nonisothermal processes are involved, the products are hotter than the reactants and any product recirculation will tend to increase the temperature at the initial stages of the reaction. Such an increase in the initial temperature would bring about a substantial increase in the initially slow reaction rate and would result in a significant speeding up of the overall reaction rate [Karim and Zhou, 1993b].

Although steam reforming does not require expensive feed components, it requires expensive and hard to maintain equipment to transfer the necessary heat to the reaction zone at a high temperature level [Cox and Williamson, 1977]. Due to the presence of catalysts, if feed stock contains sulfur bearing impurities, the reforming step must be preceded by desulfurization step to avoid poisoning of the sulfur sensitive reformer catalyst.

The partial oxidation of methane involves exothermic overall reactions [Karim and Zhou, 1993a]. The heat required to enable the reaction to proceed is generated internally by combustion of a small part of feed. Possible oxidants for conversion of methane to produce various products for different purposes are pure oxygen, oxygenated air, air, a steam-oxygen mixture, or a steam oxygenated-air mixture. The process is favored by very high operational temperatures. The oxidation process may be made to produce simultaneously with the hydrogen/synthesis gas, mechanical and/or electric power,

especially in relatively small units [Karim and Zhou, 1993a].

Some valuable intermediate products, i.e. acetylene and aldehyde, can survive the partial oxidation process through controlled mixing and quenching within the combustion zone while the conversion efficiency to hydrogen remains high [Hughes et al.,, 1991].

To ensure good conversion of the feed, higher temperatures of orders of 1700 ^{0}K are needed [Mungen & Kratzer 1951]. The equivalence ratio has a direct effect on the reaction temperature of the process. In order to raise the temperature for a higher conversion of methane and faster reaction rates, the oxygen concentration in the feed must be increased so that more heat is released by methane reacting with the relatively excess oxygen. However, this increase in oxygen consumption will reduce the relative yield of hydrogen and CO. Therefore, it is important that a suitable amount of heat be supplied because the temperature at which conversion is carried out is the most important factor influencing the reaction rate and establishing whether the conversion can be achieved within economic and practical times.

It is evident from the literature review that investigation has been going on in the field of conversion of methane into useful chemicals and fuels since the beginning of the century. Some commercial processes have been developed successfully and are in operation world-wide like methane-steam reforming. Investigators have been trying to develop two stage process for catalytic conversion of the natural gas into useful products. Latest research

indicates a shift towards one-step processes like DMTM (direct methane to methanol). So far none of the investigators has investigated the non-catalytic partial oxidation of sour natural gas process for conversion into useful products. No reference has been found in the literature regarding non-catalytic partial oxidation of sour natural gas.

CHAPTER 3

THEORETICAL BACKGROUND

3.1 Partial Oxidation

The actual reaction mechanism of the partial oxidation of sour natural gas is complex, but the behavior is consistent with a two-stage reaction mechanism, as shown in Figure 3.1 involving complete combustion of some of the methane and all of the hydrogen sulfide in the first stage via highly exothermic reactions [Eastman, 1956]. The large values of the equilibrium constants of these reactions as shown in Table 6.1 indicate that these reactions goes to completion.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad 3.1$$

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \qquad 3.2$$

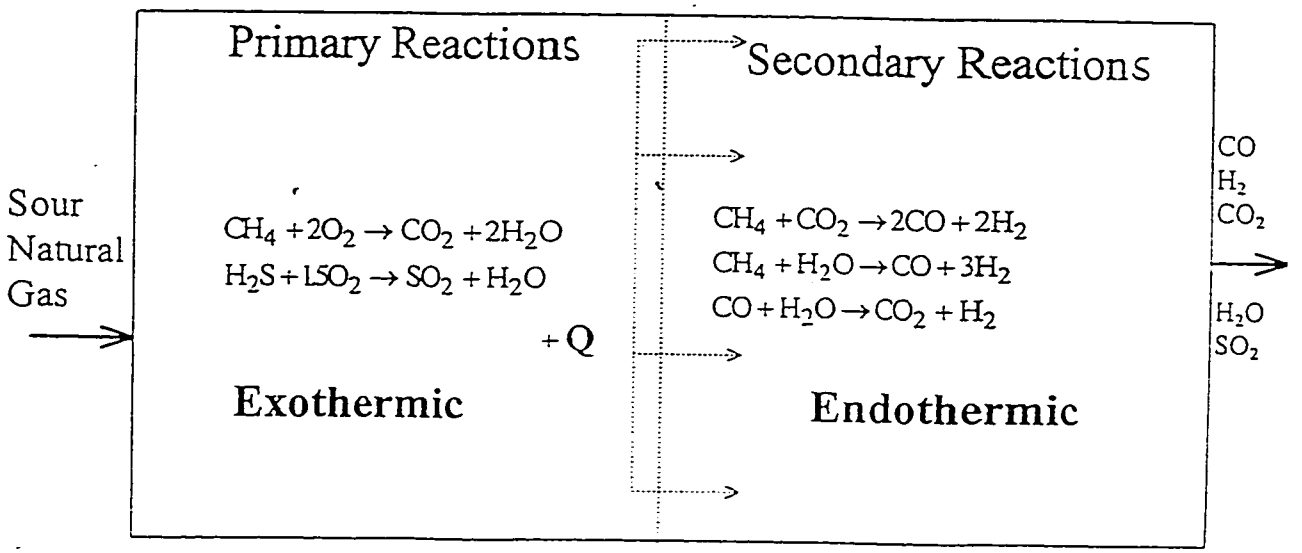


Figure 3.1 Conceptual illustration of two-stage mechanism of the non catalytic partial oxidation of sour natural gas (proposed)

After the primary reactions a large surplus of methane remains unreacted. This surplus methane then reacts with either of the products of primary reaction in the second stage as follows

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad 3.3$$

$$CH_4 + H_2O \rightarrow CO + 6H_2 \qquad 3.4$$

Whereas the primary reactions 3.1 and 3.5 are highly exothermic, both of the above reactions 3.3 and 3.4 are highly endothermic [Eastman]. The excess heat liberated in the primary reactions is supplied to the secondary reactions. Hence, the reactions are self-regulating (Autothermal). Equilibrium is very far to the right of these reactions 3.3 and 3.4 and no measurable amount of oxygen remains. In addition to these reactions of methane, the products can react via the exothermic water gas shift reaction,

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad 3.5$$

The overall reaction is

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad 3.6$$

These reactions can be classified into two categories as shown in the Figure 3.1. Reactions 3.1 and 3.2 are primary reactions. Since the temperature is so high the equilibrium lies far right [Eastman, 1956].

Experimental work carried out by Eastman [1956] has shown that free oxygen is not a component of the product and the partial oxidation is characterized by presence of carbon monoxide and hydrogen with carbon dioxide and water vapor in very small traces.

If air is used as an oxidant for partial oxidation of the sour natural gas, there is a problem of oxidation of nitrogen present in the air and production of nitrogen oxides. However, the oxidation of nitrogen takes place at the temperatures above 2700 ^{0}F [Karim and Zhou, 1993a]. Thus, it is extremely necessary to maintain the temperature of the combustion chamber below 2200 ^{0}F.

The dissociation of the steam and carbon dioxide is another possibility. However, these two reactions also takes place at temperatures above 2400 ^{0}F [Perry, 1973]. Thus, the temperature of the combustion chamber should be maintained below 2200 ^{0}F.

3.2 Absorption of SO_2 by Water

In the proposed process production of synthesis gas by non catalytic partial oxidation of sour natural gas as shown in Figure 4.1, effluent synthesis gas from the combustion chamber contains some SO_2 which is absorbed by water in a column. In the process of dissolution of gases in liquids, entropy and energy considerations act in different directions. As molecules are more disordered in a gas than in solution, the drive to achieve greater disorder tends to inhibit dissolution of gas in a liquid. On the other hand, the drive to reduce energy generally favors dissolution, so the solution of a gas in a liquid is an exothermic process. Assuming that two gases have the same enthalpy of dissolution, the one with the largest entropy will tend to be most soluble. The solubility of a gas decreases with rise in the temperature of the system [Astarita et al., 1983].

The dissolution of the SO_2 in the water is a physical absorption process. Upon dissolution of SO_2 in the water, the following reactions occur :

$$SO_2 + H_2O \leftrightarrow H_2SO_3 \qquad 3.7$$

$$H_2SO_3 \leftrightarrow HSO_3^- + H^- \qquad 3.8$$

K_1 is the equilibrium constant for the reaction (3.7).

$$K_1 = \frac{[H_2SO_3]}{[SO_2][H_2O]}$$

As the liquid phase is a dilute solution, $[H_2O]$ is a constant. It follows that

$$[H_2SO_3] \leftrightarrow (K_1\,[H_2O]\,)\,[SO_2]$$

where the quantity in round brackets is a constant.

Let α be the total concentration of SO_2 in the liquid,

$$\alpha = [SO_2] + [H_2SO_3] + [HSO_3^-]$$

If only reaction 3.7 takes place then $[HSO_3^-] = 0$ and therefore,

$$\alpha = [SO_2] * (\,1 + K_1\,[H_2O^-]\,)$$

According to Henry's law,

$$p^* = H_{SO_2}\,[SO_2] = H\,\alpha$$

where the "apparent" Henry's constant H is

$$H = \frac{H_{SO_2}}{1 + K_1\,[H_2O]}$$

Reactions 3.7 and 3.8 can be written as

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^- \qquad 3.9$$

Let K be the equilibrium constant of the reaction 3.9 (dissociation constant for sulfurous

acid) :

$$K = \frac{[HSO_3^-][H^+]}{[SO_2]}$$

For reaction 3.9,

$$[HSO_3^-] = [H^+] = \sqrt{K[SO_2]}$$

The total concentration is given by

$$\alpha = [SO_2] + [H_2SO_3] = \frac{p^*}{H} + \sqrt{\frac{K p^*}{H}}$$

which shows that the relationship between α and p^* is not linear. Figure 3.3 (Astarita) is a plot of SO_2 solubility data which exhibits the kind of behavior predicted by the above equation.

Upon differentiation, the above equation yields,

$$\frac{d\alpha}{dp^*} = \frac{1}{H} + \frac{1}{2}\sqrt{\frac{K}{Hp^*}}$$

Which shows that, as $p^* \rightarrow \infty$, the slope of the curves in the Figure 3.3 approaches the constant value of H. This allows the extraction of the Henry's Law constant from the curved equilibrium lines.

The non linear term in equation becomes negligible when

$$p^* >> KH$$

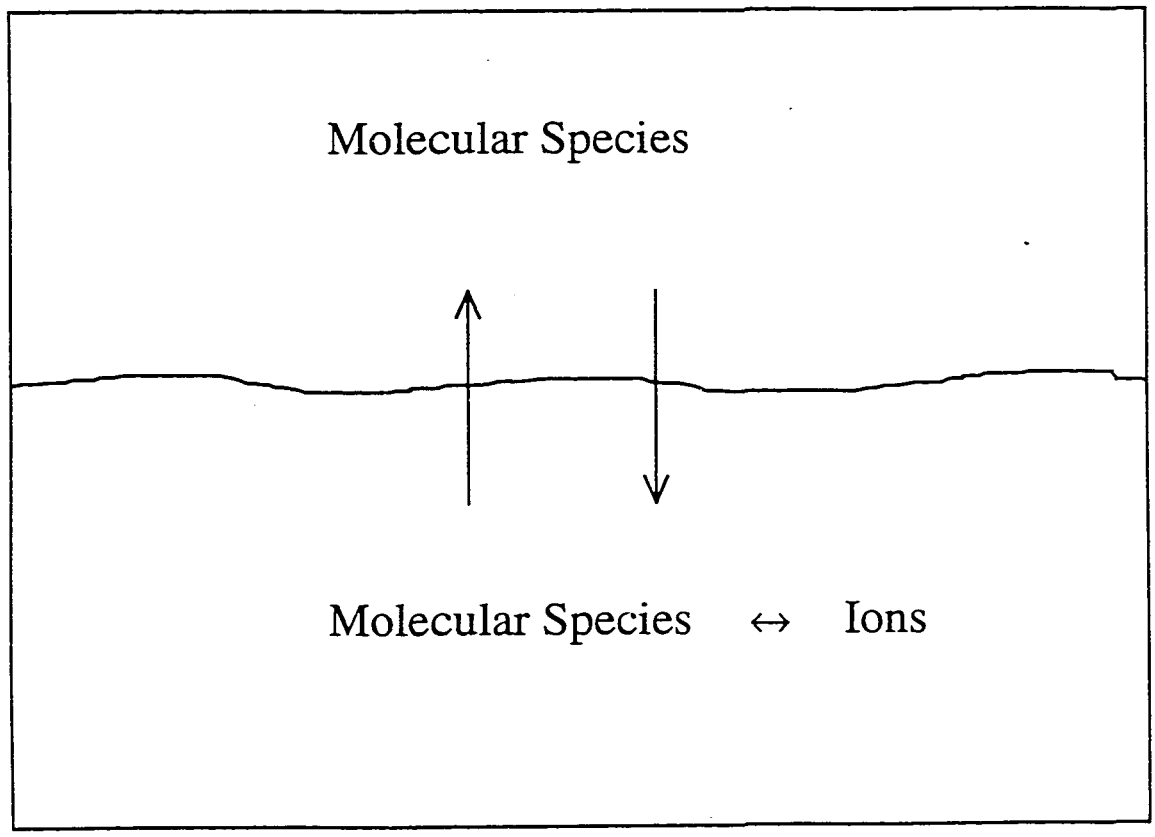


Fig. 3.2 Mechanism of absorption of SO_2 in water

The right hand side of the above equation is of the order of 10^{-2} atm and, therefore, curvature of the equilibrium line is important in the industrially relevant range of partial pressures (at 50^0 C for SO_2 , K = 1.25 * 10^{-2} gmol/liter, and H = 2 atm liter/gmol).

The solubility of the SO_2 in the water can be described for the temperature range of 283 to 386 K [Kohl and Reisenfield]

$$R \ln x_{SO_2} = A + B/T + C \ln T + DT \qquad 3.10$$

where the values of A, B, C and D are

A = -29.885 cal K^{-1} mol^{-1}

B = 5709.15 cal mol^{-1}

C = 0.601884 cal K^{-1} mol^{-1}

D = 0 cal K^{-2} mol^{-1}

The solubility of the sulfur dioxide in the water is presented in the Figure 3.4. The sulfur dioxide concentration in water is plotted against partial pressure of sulfur dioxide in the gas. It is evident from the figure that the solubility of the sulfur dioxide in the water decreases with the increase in the temperature, as predicted from the theory.

3.3 Open Sulfur-cycle Process

This is a open cycle electrochemical system also known as Westinghouse process. Since

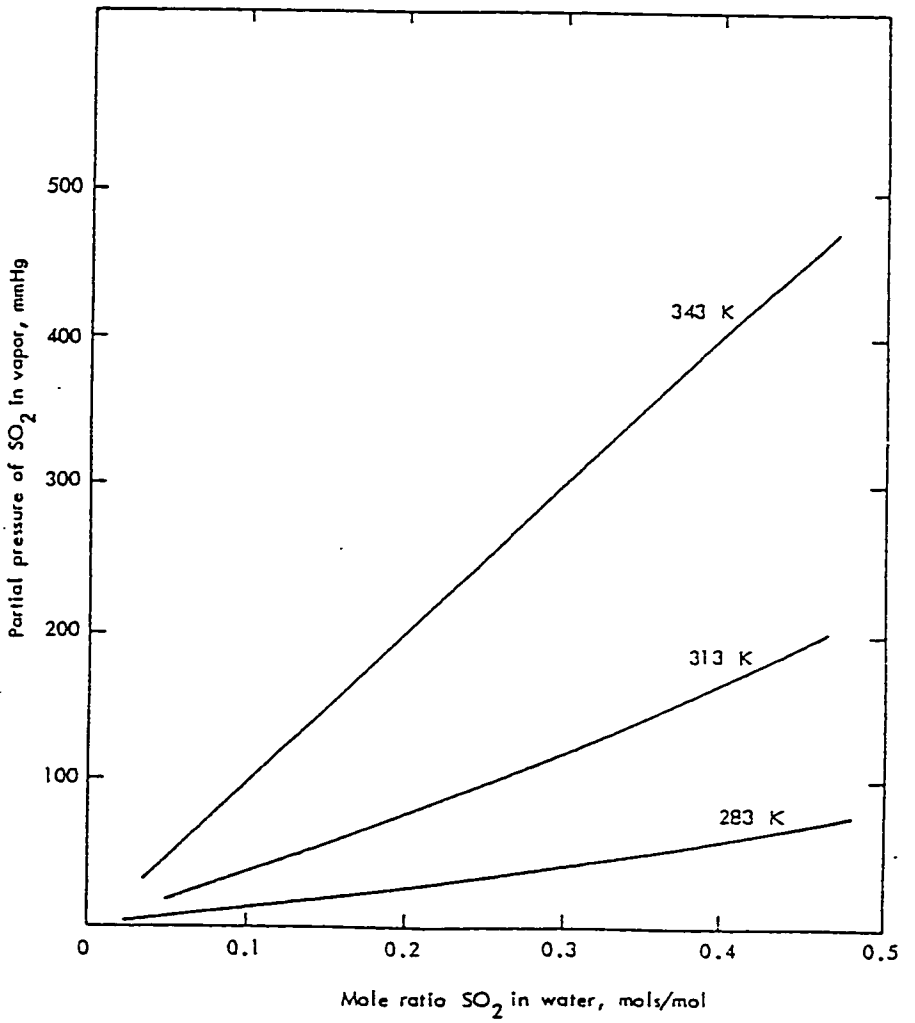


Figure3.3 Solubility of SO_2 in water [Astarita etal., 1983]

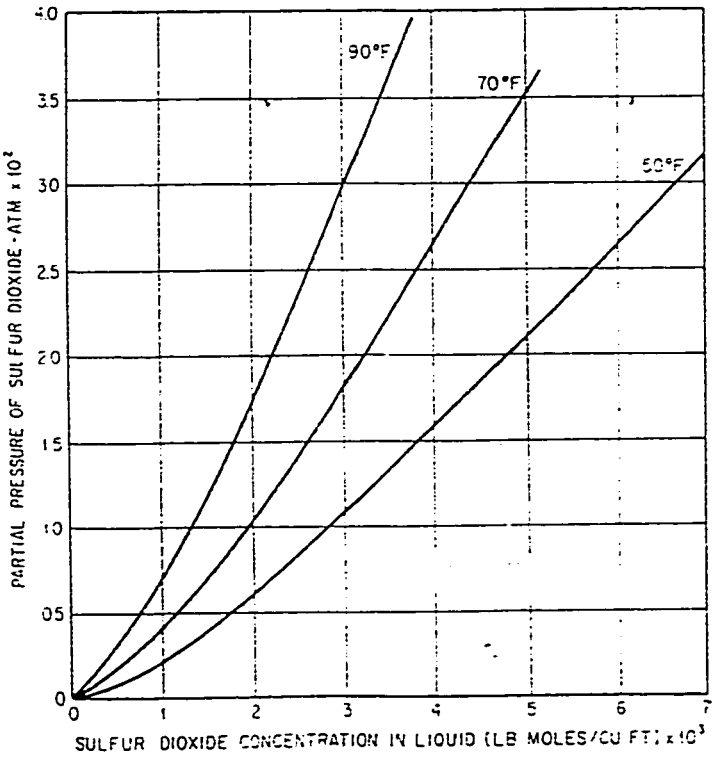


Figure 3.4 Solubility of SO_2 in water [Kohl and Reisenfield, 1988]

the supply of the SO_2 is continuous, it is more beneficial to use open sulfur-cycle instead of closed sulfur-cycle. Open sulfur-cycle is similar to closed sulfur-cycle except that decomposition of H_2SO_4 is eliminated. Hydrogen is produced in a low temperature electrochemical step, wherein sulfuric acid and hydrogen is produced from sulfurous acid, i.e.,

$$2H_2O\ (l) + SO_2\ (aq) \rightarrow H_2SO_4\ (aq) + H_2\ (g) \qquad 3.11$$

The open sulfur-cycle continuously produces sulfuric acid as a main product. The sulfuric acid produced has to be concentrated using multistage flashing before it is sold as a concentrated acid.

Electrical power required in the electrochemical step is lower than that needed for water electrolysis. The theoretical voltage to decompose water is 1.23V, with many commercial electrolyzers requiring 3.0V. The power requirements for reaction 3.11 is 0.17 Volts, which is theoretically less than 15% of that required in conventional electrolysis. The cell voltage of 600-800 mV believed to be obtainable in a practical sulfurous acid electrolyzer would only require some 30-40% of the electrical power of advanced water electrolyzers.

Hydrogen is generated electrolytically in an electrolysis cell which anodically oxidizes sulfurous acid to sulfuric acid while simultaneously generating hydrogen at the cathode.

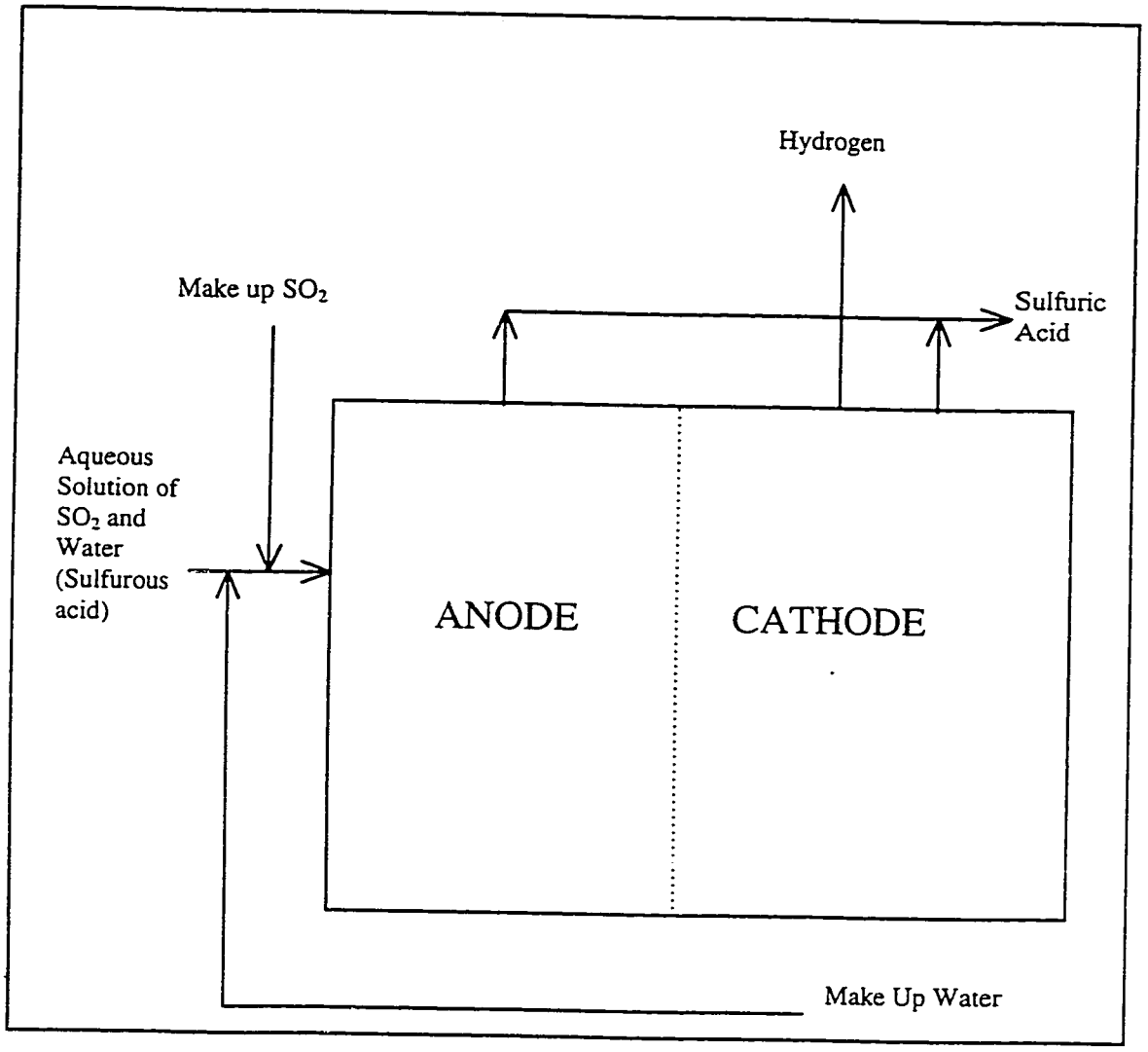


Fig. 3.5 Schematic diagram of the Open Sulfur Cycle Process

CHAPTER 4

PROCESS DESCRIPTION

4.1 Preheating

Description

Sour natural gas and oxidant are preheated separately prior to the partial oxidation. Because sour natural gas undergoes cracking above 1200 ^{0}F followed by the deposition of carbon, and oxidant is highly reactive above 1000 ^{0}F, which is highly undesirable, sour natural gas is preheated only up to 1200 ^{0}F and oxidant is preheated only up to 1000 ^{0}F. The maximum allowable preheat is limited by the ignition temperature of the gas mixture, since there is a danger of flashback to the mixing zone.

Another method to improve the overall thermal efficiency of the process is by preheating the feedstock through heat exchange with the product gases.

The preheating is carried out separately for the sour natural gas and the oxidant. The preheating is carried out separately:

- To avoid complete combustion
- To avoid formation of carbon/soot
- To avoid explosion in the preheater
- To avoidside reaction
- To avoid flame in the supply pipes
- To stay in the safe limits of inflammability

Equipment

Preheating could be carried out in three ways :

- Using heat exchangers. By utilizing sensible heat of effluent gases of the partial oxidation combustion chamber or by using steam generated by the use of exhaust gases of combustion chamber.
- By directly inserting coils in the combustion chamber in which feed gas is preheated by heat of the exothermic reactions of the partial oxidation.
- Using gas fired furnace.

4.2 Premixing

Description

The sour natural gas and the oxidant are intimately premixed in the proper proportions in the burner. This is carried out to avoid

- Hot spots in the combustion chamber

- Residual natural gas in the combustion chamber effluent
- Thermal decomposition of the sour natural gas
- Coke formation
- Explosion (in case pure oxidant comes in the direct contact of the combustion chamber wall)

Equipment

Burner

4.3 Partial Oxidation

Description

The sour natural gas and the oxidant should be thoroughly mixed as soon as they are introduced into the combustion chamber, prior to the partial oxidation. This is essential to prevent thermal decomposition and coke formation. The mixing is achieved in a specially designed alloy burner with in the reaction zone.

Figure 4.1 shows the schematic diagram of non-catalytic partial oxidation of sour natural gas. The non catalytic reaction of CH_4 and O_2 proceeds as a flame. All of the oxidant is consumed in the process. H_2 and CO are the major components of the combustion chamber effluent gas. The mechanism of the reactions is very complex but this behavior is consistent with a stage combustion chamber

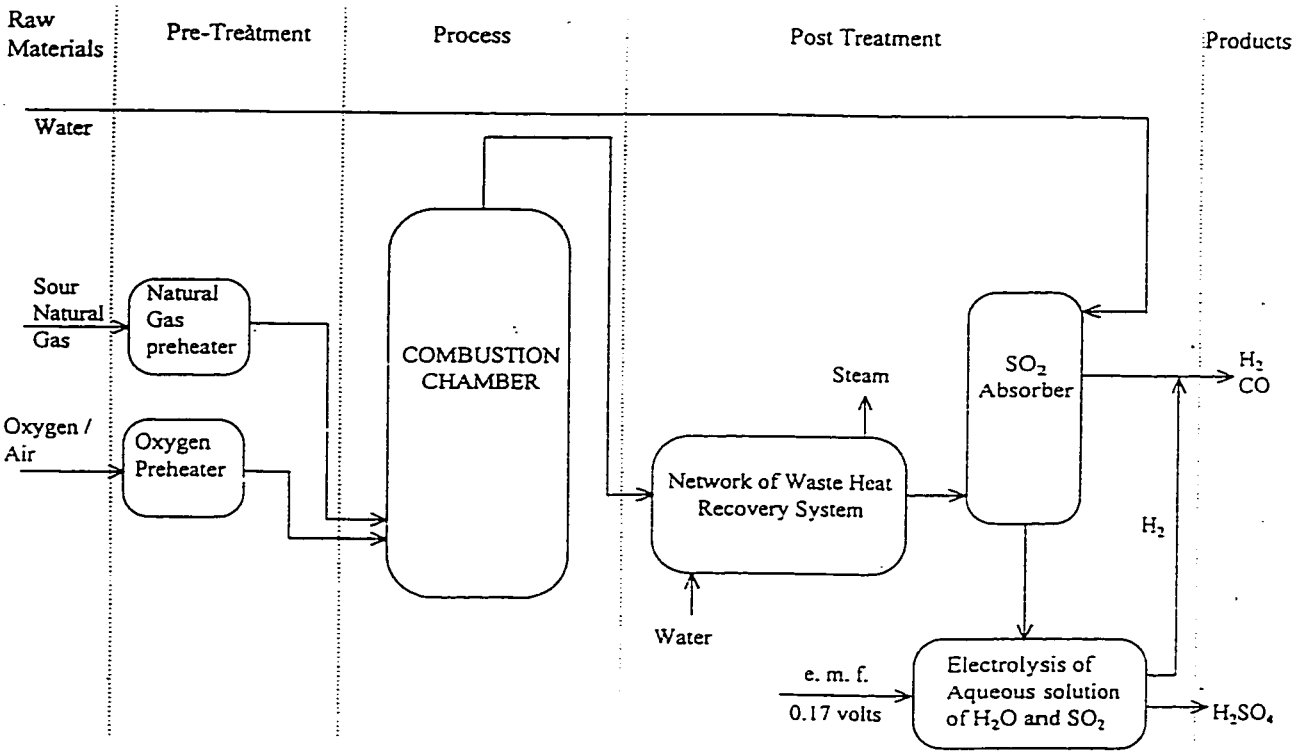


Figure 4.1 Schamatic diagram of proposed process of non catalytic partial oxidation of sour natural gas

mechanism involving complete combustion in the first stage via highly exothermic reactions 3.1 to 3.2 [Eastman]. A large surplus of methane remains unreacted. This surplus methane can then react with either of the products of the primary reaction by reactions 3.3 and 3.4. Equilibrium is very far to the right of reactions 3.3 and 3.4 and no measurable oxidant remains. Whereas the primary reaction are highly exothermic, both of these reactions are highly endothermic. The excess heat liberated in the primary reactions is supplied to the secondary endothermic reactions. The balance between these exothermic and endothermic reaction is such that a departure from equilibrium in the secondary stage has the effect of liberating heat. This increases the temperature and tends to accelerate the secondary reactions. Thus, the reaction system is self regulating (Autothermal). In addition to these reactions of methane, the products can react via exothermic water gas shift reaction 3.5. The desired overall reaction is reaction 3.6.

The disadvantages of pressure operation lie in the adverse effect on equilibrium and the severe mechanical problems that will be introduced in this high temperature process.

As the ratio of carbon to hydrogen in the fuel is increased a point is reached at which the quantity of oxidant necessary to react with the carbon is more than enough to bring the product mixture to the necessary temperature. At this point steam can be added to supply part of the total oxidant and to hold the reaction temperature at the desired level.

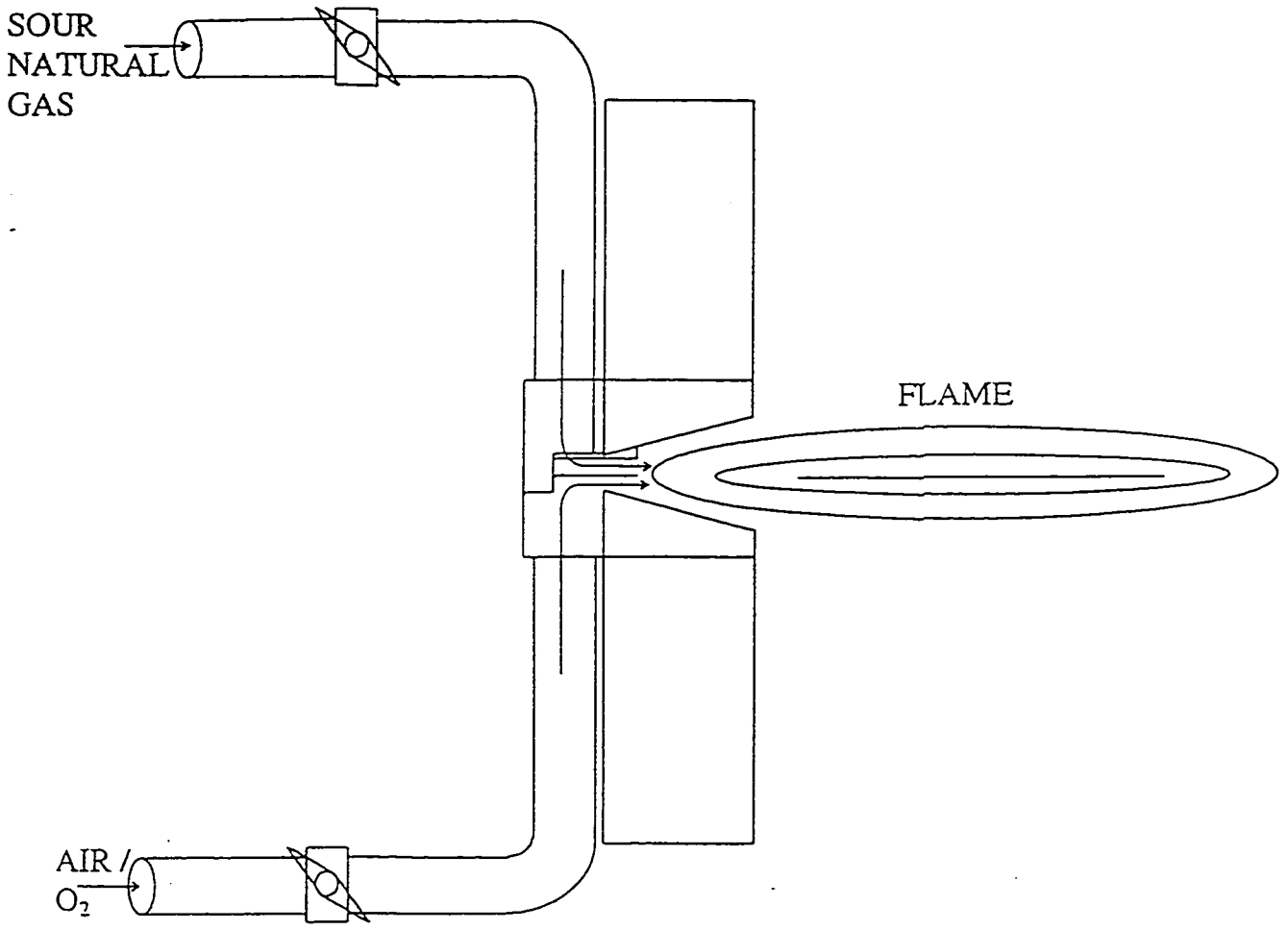


Figure 4.2 Schematic diagram of the burner of the combustion chamber [Dotterweich, 1969]

Equipment

Burner

An alloy burner of carefully controlled dimensions with uncooled refractory is used in order to reduce heat loss and avoid dependence on coolant supply. A system II type of nozzle mixing burner is used as shown in Figure 4.2, in which the sour natural gas and oxidant are kept separate until discharge from the burner into the combustion chamber. It is generally used with low pressure gas (up to 15 psig) and low pressure air (up to 15psig) [Dotterweich, 1969]

This very simple and flexible system can be used in industries at 1000° to 2200° F, with combustion chamber heat release up to 250 M Btu per cu. ft. The Ratio control may be either mechanical (operating valves in both the oxidant and gas lines) or proportioning (arranging for variations in one fluid to initiate proportionate variations in other). By suitable variation in the burner and control equipment, a nozzle mixing system can be operated either stoichiometrically or with excess oxidant or excess gas as required, without possibility of flashback. Usually the burner system is sealed so that all air is controlled by either a manual or an automatic ratio control system as shown in Figure 4.2.

Combustion Chamber

The combustion chamber used to carry out non catalytic partial oxidation reactions is a vertical, steel pressure vessel with multi-layered refractory lining [Shearer and Kuhre, 1980]. There are no internal baffles or catalyst beds. Preheated hydrogen feedstock and

oxidant should be fed under precise flow control to the specially designed combuster. The oxidant along with the hydrogen feedstock enters the combustion chamber in the form of vortex spray in the combustion zone. The multiple layer refractory lining is designed to withstand the high temperature in the combustion chamber. A commercially available refractory, firebrick is used for this purpose. Equipment must be designed to withstand temperatures above 2000^0 F. The very severe condition of temperature above 2000^0 F should be met through the use of internally insulated combustion chambers. These are designed with cylindrical carbon-steel pressure shells lined with successive layers of specially selected refractories.

The inner wall of the combustion chamber can withstand temperatures approaching 2500^0 F, in case of control failure. However, in normal operation the refractories are subjected, only to temperatures that are allowable for firebricks.

Adequate heat exchange between the exothermic primary reactions and endothermic secondary reactions should be provided. It is also essential to avoid contact between hot, unreacted oxidant and the combustion chamber wall, as this is highly destructive. Excessive local temperature can damage the refractory, hence it is imperative that all reactants be intimately mixed. Care must also be exercised to provide for the differential expansion of the refractory and the external pressure shell and at the same time to prevent the access of hot gases to the metal surface. The temperature ranges from 1700^0 F to 2200^0 F. No catalyst is used. The reactions are autothermal.

Table 4.1 Composition of austenitic steels [Perry, 1973]

Type	Cr	Ni	Fe	Other
304	18	8	Balance	-
321	18	10	Balance	Ti
347	18	11	Balance	Cb
316	18	12	Balance	Mo
309	24	12	Balance	-
310	25	20	Balance	-
330	15	35	Balance	-

In Canada, hydrogen sulfide gas is oxidized to get elemental sulfur and hydrogen. Special materials are used to make the combustion chamber. Some of these materials are given below [Paskell, 1983].

Material for Construction

1. Chromium
2. Aluminum and its alloys
3. Inconel 600 80% Ni 16% Cr 4% Fe
4. Austenitic allloy Steel presented in Table 4.1.

Refractory Material

1. Firebrick
2. Silica Brick SiO_2 95% Fusion Point 3100^0 F

4.4 Waste Heat Generation

Description

An important feature of this process is the capability of recovering much of the heat in the combustion chamber product gas by generating high-pressure steam. The hot gas from the combustion chamber flows directly to a waste-heat exchanger of special design where it passes through helical coils mounted in the exchanger shell. The sum of the sensible heat recovered from the combustion chamber effluent gas (by raising steam) plus the potential

heat of combustion represented by the product gas itself is equal to about 95% of the hydrocarbon feedstock heating value (GHV). The use of helical tubes and proper gas velocity gives very long service life without the need for periodic cleaning and without impairment of heat transfer. The steam is generated at a pressure at least 150 psi greater than the combustion chamber pressure so that it can be used directly as moderating steam. Waste-heat exchangers for the partial oxidation process could be designed for steam pressures to about 1500 psig.

The gas leaves the waste-heat exchanger at a temperature somewhat greater than the generated steam temperature. Additional heat is recovered from the gas in an economizer by heat exchange with feedwater for the waste-heat exchanger. The split of heat recovery duties between the waste-heat exchanger and the economizer is optimized during the design phase of the partial oxidation process.

A critical factor in the manufacture of the hydrogen and/or synthesis gas is its energy consumption. Since the partial oxidation reactions are highly exothermic, it is obviously desirable to recover as much of the heat as possible in a useful form and to use it so as to approach an adiabatic overall process. An integrated auxiliary water-heat boiler is employed to produce moderating steam for adjusting the H_2 to CO ratio or for the production of power and/or heat which might offset the power and heat requirements.

Another method to improve the overall thermal efficiency of the process is by preheating the feedstock through heat exchange with the product gases and by improving the combustion chamber insulation to produce higher operating temperatures since higher operating temperature favors the endothermic reforming reaction. The preheat temperature is limited. It is limited by two factors. First is the design of the preheater, which should be such that there are no local hot spots or stagnant pockets where methane will decompose. The second is the temperature at which spontaneous ignition will occur when the oxidant and methane is premixed.

Equipment

1. Integrated auxiliary water-heat boiler
2. Economizer

4.5 Absorption System

Description

The effluent gases of the combustion chamber are scrubbed by water. The operation is carried out counter-currently. The water is fed from the top and the effluent gases from the combustion chamber is fed from the bottom of the absorption tower. An aqueous solution of the sulfur dioxide (sulfurous acid) will be formed. This solution is a feedstock to the open sulfur-cycle or modified Westinghouse process. Sulfur dioxide will be dissolved in water in accordance with Henry's law.

Equipment

A packed bed tower is employed to provide sufficiently large interfacial surface between water and gases. The tower should be packed with raschig rings, intalox, saddle or pall rings.

4.6 Open Sulfur Cycle Process

The SO_2 is continuously produced as a by-product by the process of non catalytic partial oxidation of the sour natural gas. It is utilized to manufacture sulfuric acid using open sulfur-cycle. Open sulfur-cycle is similar to closed sulfur-cycle except that decomposition of H_2SO_4 is eliminated. Hydrogen is produced in a low temperature electrochemical step, wherein sulfuric acid and hydrogen is produced from sulfurous acid as shown in the reaction 3.11.

Since the supply of SO_2 is continuous the open sulfur-cycle would continuously produce sulfuric acid. The produced sulfuric acid has to be concentrated using a multi-staged flashing before it is sold as a concentrated acid.

The open sulfur cycle or Westinghouse process is explained in section 3.3.

CHAPTER 5

SIMULATION PROCEDURE

5.1 Simulation using ASPENPlus

ASPEN stands for **A**dvanced **S**ystem for **P**rocess **E**ngineering. ASPEN is a state-of-art process simulator, chemical process design tool. The 15,000 line computer program simulates the flowsheet of a proposed or operating plant; ASPEN calculates detailed heat and material. The project was funded by department of energy, USA and developed by MIT.

Apart from the general simulation capabilities, ASPEN has certain advanced engineering capabilities, which includes the ability to compute the properties of coal and coal derived materials and great flexibility for the user to add specialized models or other computations.

In addition to handling the conventional vapor/liquid process operations, the ASPEN library of process models includes solids handling and separations units, a set of generalized reactors, improved flash and distillation unit models and process models from FLOWTRAN simulator. ASPEN includes data banks from which the required physical property constants and correlation parameters can be retrieved automatically at run time. Comprehensive data on more than 100 coals covering a wide range of ranks and geographical parameters is included.

ASPEN Structures

- The executive system
- Computational architecture
- Data for streams and equipment models
- Physical property monitors and others

Executive System

Executive system is preprocessor type which develops the actual simulation program. An input translator program reads the user input and generates the FORTRAN main program for execution. The executive programs set up the data structure and generates the computing sequence of equipment models. This structure allows

1. a larger and variable number of model program to be executed.
2. FORTRAN statements to be included for execution.
3. The need for only a minimum amount of memory for the simulation in executing an ASPEN calculation.

ASPENPlus executive system

- Reads the input data
- Initializes the variables used in the calculations
- Arranges the order of calculations to correspond to the connection of the process units
- Calls for thermodynamic packages as it is needed
- Converges the recycle calculation
- Prints output results
- Repeats the calculations for parametric case studies.

Computational Architecture

Computational architecture is sequential modular approach with advanced feature. To model a process, each equipment module is simulated by a program module. The overall process is simulated by connecting the models together in the same way as the equipment in the flowsheet. When input streams are known, then outputs are calculated. The entire flowsheet can be calculated "sequentially" in this manner.

Data of Streams and Equipment Models

ASPEN utilizes a plex data structure. Information is stored in blocks of contiguous locations known as beads. Beads of any length are created dynamically from pools for free storage which may be thought of as a lengthy FORTRAN array. The combination of preprocessor approach and plex data structure has resulted in absence of dimensional constraints on the system. There are no maximum number of streams, components, models, stages in column etc. except as limited by the total memory available.

Equipment Subroutine

Unit Operations and Streams

One of the time-consuming feature of process design is the calculation of the sizes (costs) of the process engineering, once the stream flow rates, temperatures, and pressure have been specified. This effort is even more tedious if trial and error procedures are used to determine the stream flows or temperatures because of the presence of recycle loops. The computer can solve these trial and error calculations relatively rapidly so that it is an ideal tool to use to improve the estimates for material balances and to solve complicated sets of equipment design equations.

Three kinds of equipment design equations are supplied to the program to use the equipment subroutines

- The type of design equations to solve
- The order of connection of various process units
- Design parameters for the particular unit under consideration

A library of generalized models is supplied in ASPEN to allow the user to simulate chemical and petroleum processes (presented in Table. 5.1). Although the ASPEN process models can be put together to simulate many types of processes, it may still be necessary to use specialized or proprietary models. The ASPEN system facilitates the inclusion of user's own model either in FORTRAN source code or compiled into object code. The

proprietary model may rely on the entire physical property system to calculate the required properties; however, the user routines must have the correct interface calls.

INPUT LANGUAGE

The ASPEN input language is oriented towards process engineers familiar with chemical engineering calculations, but without extensive knowledge of computer programming. The input can be considered to be made up of paragraphs, sentences and words. A paragraph begins with a primary keyword and may consist of one or more sentences. Each sentences begins with a secondary keyword that indicates the category of data appearing in the sentence. Tertiary keywords are used to enter data and their values are the data items. For example, in the following statement

```
BLOCK       F1      FLASH2
      PARAM       TEMP = 310  PRES  = 1(ATM)
```

The word BLOCK is a primary keyword indicating that the paragraph contains block data. The user specified block identifier is F1 and the unit operation model FLASH2 is a two phase flash with specified temperature and pressure. PARAM is a secondary keywords indicating that the sentence contains block parameters. TEMP and PRES are tertiary keyword which may consist of a single data item or a vector of values.

The internal units for calculation are basic SI units, but the user may specify optional sets of input and output units which includes english engineering, metric engineering or SI

units. In addition, the user may specify individual units, such as temperature, that override the set.

The input is completely free format except that primary keywords must begin in column 1. The order of input language is sorted into a standard order before processing. Although every data item or vector of items has a tertiary keyword, the keyword may be omitted to allow positional input. The default principle is fully exercised and wherever it is meaningful, default values are provided for items the user need not supply.

There are some advanced features for design specification. The DES-SPEC paragraph shows how variables in the problem can be defined, in a DEFINE statement, to be FORTRAN variables which can be used in any FORTRAN statements to define any arbitrary function. Then, any other problem variable can be varied, in a VARY statement, to drive the function to zero. This flexibility in design specifications is quite powerful.

FORTRAN statements also can be inserted by the user in the paragraph called FORTRAN. Using the DEFINE sentence, any problem variables may be accessed. Using FORTRAN language, any arbitrary transformation of the problem variables may be made and stored. This extremely flexibility allows the user to

1. Modify block calculations
2. Change stream values

3. Insert user FORTRAN blocks
4. Execute many other powerful specific functions

One before and one after statement can be used to make the FORTRAN execution before or after any block.

For convergence calculation ASPEN employ some advanced features with the well-proven sequential modular architecture. In many process simulations, the user is responsible for structuring all computational sequence directly. In ASPEN the system is capable of complete automatic determination of the computational sequence. The user can select certain tear streams and can easily specify the entire sequence.

In addition, convergence calculation may be combined simultaneously with design specification. The usual methods would be to embed the design in a convergence loop and meet the design specification in each recycle calculation. A quasi-Newton method convergence calculation in ASPEN will allow a simultaneous, more efficient solution for the more difficult problems.

Another potential advancement is permitted in ASPEN system. Tear streams can be designated so that a user might define blocks or series of blocks and simulate these sets as quasi-linear blocks. The convergence method could utilize this information and solve the material (or energy) balances explicitly. In this way, a simultaneous modular architecture could be utilized.

Physical Property

One of the tedious tasks in the process design is looking up data for the physical properties of the compound of interest, and using these properties to compute the vapor-liquid relationships, the enthalpies of the process streams etc. It is possible to add similar data for other compounds and to determine the constants of interest directly from the experimental data. These data for pure components are adequate to predict the thermodynamic properties of the mixtures encountered in the process streams, provided that the mixtures satisfy the assumption of ideal or regular solution theory. For more complex mixtures it is necessary either to supply estimates of the liquid-phase activity coefficients. The physical property monitors of ASPEN provide very complete flexibility in computing physical properties. Quite often a user may need to compute a property in one area of a process with high accuracy, which is expensive in computer time, and then compromise the accuracy in another area, in order to save computer time. In ASPEN, a user can do this by specifying the method or "property route", as it is called. The property route is the detailed specification of how to calculate one of the ten major properties for a given vapor, liquid, or solid phase of a pure component or a mixture. Properties that can be calculated are enthalpy, entropy, free energy, molar volume, equilibrium ratio, fugacity coefficient, viscosity, thermal conductivity, diffusion coefficient, and thermal conductivity. ASPEN provides a state-of-the-art capability for thermodynamic properties of conventional components. A number of equation-of-state (EOS) models are supplied to handle virtually any mixture over a wide range of temperatures and pressures. The

equation-of-state (EOS) models are programmed to give any subset of the properties of molar density, residual enthalpy, residual free energy, and the fugacity coefficient vector for a liquid or vapor mixture. Some of the EOS models made available in ASPEN are the following :

1. Hayden-O'Connell Second Virial Coefficient
2. Redlich-Kwong
3. Redlich-Kwong-Soave
4. Peng-Robinson
5. Lee-Starling (modified Benedict-Webb-Rubin)
6. Prausnitz Perturbed-Hard-Chain

Correlations for activity coefficients can be selected from the following :

1. Extended Scatchard Hildebrand
2. Modified van Laar
3. Wilson
4. Modified NRTL
5. UNIQUAC
6. Margules (for water-hydrocarbon systems)

Similarly, other property calculations may have a variety of models to choose from.

The physical property system is supported by a data file on both conventional compounds

and on typical coal analyses and data. The data bank contains correlation constants for over 400 conventional compounds and extensive data for thirteen characteristic coals. A data file management system permits a user to modify the data files, to create his own private data files, and to allow the system to automatically call in these data for a simulation run. Another stand-alone system planned with ASPEN is the Data Regression system. This allows the user to determine the correlation constants, from any of the system property correlations, to fit experimental data. It is expected to be widely used for vapor-liquid equilibria fitting.

BWR-LS Property Option Set

BWR-LS is based on the BWR-Lee-Starling equation of state which is a virial-type equation. The equation of state is used to calculate all thermodynamic properties resulting in self-consistency among the properties. It is comparable to PENG-ROB, RK-SOAVE and LK-PLOCK for phase equilibrium calculation, but is more accurate than PENG-ROB and RK-SOAVE for liquid molar volume and enthalpy (Starling and Han 1971; Starling and Han, 1972).

BWR-LS requires critical parameters such as critical temperature as input. There are also optional binary parameters. However, for accurate results in equilibrium calculations (VLE and LLE), the binary parameters are required. The binary parameters can be determined from experimental phase equilibrium data, usually binary data, using the ASPENPlus Data Regression System (DRS). Built-in binary parameters are available for a

large number of component pairs on the properties parameters Binary Scalar form.

Mixture Types

BWR-LS is applicable to nonpolar or mildly polar mixtures including light gases such as carbon dioxide, hydrogen sulfide, hydrogen and so on. BWR-LS is particularly suitable in the high temperature and high pressure regions, such as in hydrogen processing applications or in supercritical extractions. Example applications include natural gas processing and refinery simulations.

Range

Reasonable results can be expected at all temperatures and pressures. BWR-LS is consistent in the critical region; therefore it does not exhibit anomalous behavior, unlike the activity coefficient option sets. However, results are least accurate in the region near the mixture critical point.

Advanced Capabilities

- ASPEN has many feature, which qualify it as a state-of-the-art process simulator. A flexible executive system allows the user to have unlimited numbers of dimensions in streams, components, models and stages in equipment models. Solids may be handles in as many phases as desired. Arbitrary properties, called attributes, many be given to these phases and streams to allow handling properties such is particle size distributions. The features of FORTRAN insertion, design specifications and convergence options give ASPEN some extremely flexible and powerful simulation

Table. 5.1 Unit Operation models in ASPEN

MIXER	Solids handling
General Mixer	Cyclone
Splitters and Separators	Electrostatic Precipitator
Flow Splitter	Fabric Filter
Substream Splitter	Venturi Scrubber
Two Product Separator	Crusher
Substream Attribute Separator	Screen/Classifier
Pressure Changers	Hydrocyclone
Pump/Slurry Pump	Rotary Drum Filter
Compressor/Expander	Filtering Centrifuge
Heaters and Heat Exchangers	Moving Bed Dryer
Heat Requirement Heater	Fluid Bed Dryer
Duty Specified Heater	Reactors
Heater for a vapor fraction	Yield-Based Reactor
Cooler/Condeser	Fractional Conversion Reactor
Direct Contact Heater/Cooler	Combined Specificatipon Reactor
Flash Models	Well-stirred Reactor model
Two phase Flash	Plug-flow Reactor model
Three Phase Flash	Two Phase Chemical Equilibrium
General Flash	General Phase and Chemical Equilibrium
Distillation	Stoichiometric Reactor
Shortcut, Design	Stream Manipulators
Shortcut, Rating	Multiplier
Rigorous, Distillation, FRAKB	Class Changer
Rigorous, Absorption, ABSBR	Duplicator
Rigorous, Separation, RADFRAC	Phase Separator
Minimum Reflux, MINREF	Phase Mixer

capabilities. A library of state-of-the-art unit operations calculations is available. Physical property correlations for conventional components and coals give a wide variety of the best methods for the user. An extensive data bank for physical properties is made automatically available to a user and he may create his own private data bank. A thorough costing and economic evaluation system allows the user to assess the values of a flowsheet in dollars on a consistent basis.

MODEL

RSTOIC

Stoichiometric Reactor

Rstoic is used to model a reactor when :

- Reaction kinetics are known or unimportant
- The reaction stoichiometry is known
- Extent/Conversion of the reaction is known

Materials Stream

Inlet	At least one material stream
Outlet	One product stream

Heat Stream

Inlet	Any number of heat streams (optional)
Outlet	One optional heat stream

If only temperature or pressure is specified on RSTOIC.main form, RSTOIC uses the sum of the inlet heat streams as a duty specification. Otherwise, RSTOIC uses the inlet heat stream only to calculate the net heat duty. The net heat duty is the sum of the inlet heat streams minus the actual (calculated) heat duty. The net heat duty could be used as an outlet heat streams.

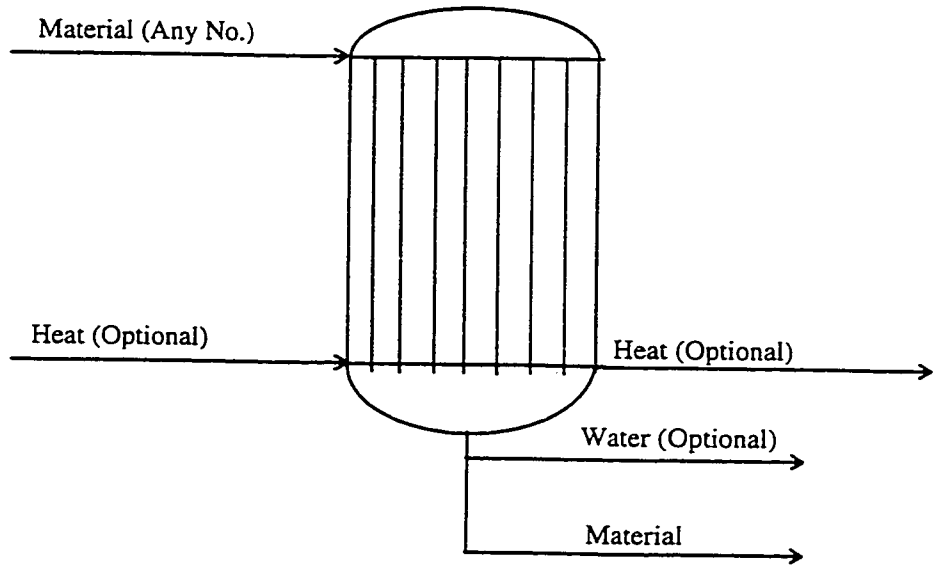
Input for RSTOIC

The RSTOIC.Main form takes

- Reactor conditions
- Whether reactions occur simultaneously or in series

The RSTOIC.Reac form takes

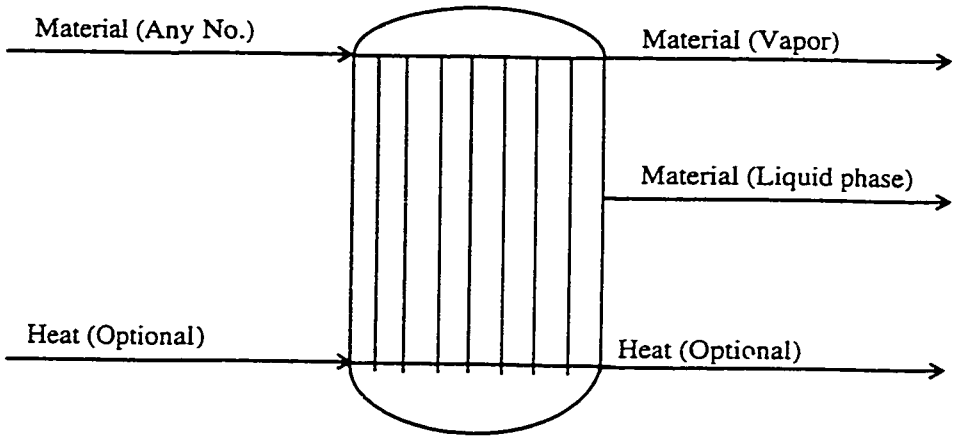
- Reaction Stoichiometry
- Reaction extent or conversion of a key component



REQUIL

Equilibrium Reactor

REQUIL is used to model reactors when some or all reactions reach equilibrium. REQUIL can calculate single-phase chemical equilibrium or simultaneous phase and chemical equilibrium. REQUIL calculates equilibrium by solving stoichiometric chemical and phase equilibrium equations.



Materials Stream

Inlet	At least one material streams
Outlet	One material stream for the vapor phase
	One material stream for the liquid phase

Heat Stream

Inlet	Any number of heat streams (optional)
Outlet	One optional heat stream

If only temperature or pressure is specified on REQUIL main form, REQUIL uses the sum of the inlet heat streams as a duty specification. Otherwise, REQUIL uses the inlet heat stream only to calculate the net heat duty. The net heat duty is the sum of the inlet heat streams minus the actual (calculated) heat duty. The net heat duty could be used as an outlet heat stream.

Input for REQUIL

The REQUIL Main form takes

- Reactor Conditions
- Reaction Stoichiometry

If no additional specifications are given, REQUIL assumes the reactions reach equilibrium. REQUIL calculates equilibrium constants from the Gibbs energy. The equilibrium can be restricted by specifying one of the following :

- Molar extent for any reaction
- A temperature approach to chemical equilibrium for individual reactions or the entire system

If temperature approach (ΔT) is specified, REQUIL evaluates the chemical equilibrium constant at T + ΔT, where T is the reactor temperature (specified or calculated).

REQUIL performs single-phase flash calculations nested inside a chemical equilibrium loop. REQUIL cannot perform three-phase calculations.

PROCEDURE

INPUT

There are two modes of input :

- GUI (graphical user interface)
- .INP file (ASPENPlus input file)

1. Input streams are drawn. Then, different required unit operation blocks are selected and drawn i.e. reactor, mixer, heater, heat exchanger etc. These unit operation blocks are connected by streams according to the flow in the flowsheet. Finally, product streams are drawn and connected. If a particular unit operation block is not available with ASPEN, then a block is created and the subroutine for the calculation for that particular unit operation block is supplied by the user.
2. Then ASPENPlus always calculates the temperature, pressure, vapor fraction, molecular weight, total flow, enthalpy, entropy and density for the simulation streams. Additional properties to be calculated by the ASPENPlus may be specified. Then, the property sets may be selected. These property sets are ASPENPlus databanks.
3. The compounds to be used in the process simulations are selected from the Component main form of ASPENPlus. If a particular compound is missing from the ASPENPlus then an entry for that compound is made by the user in the data bank and all the required properties of that compound are supplied by the user.

4. The Properties main form is used to select the thermodynamic methods used to calculate properties such as K-values, enthalpy, and density. BWR-LS (Benedict-Webb-Rubin-Lee-Starling) optionset was chosen for the simulation.
5. The Stream main form is used to supply the stream data for the streams like temperature, pressure, composition and flow rate.
6. The Block main form is used to supply the data for all the blocks, i.e. reactor is supplied with stoichiometry of reaction, temperature, pressure, and conversion.
7. The blocks are supplied with data i.e. reactor is supplied with stoichiometry of reaction, pressure, and conversion. Similarly all the blocks are supplied with required data.

Input consists of definition of :

- Components
- Flowsheet connectivity
- Feed streams
- Thermodynamic methods and transport properties
- Unit operations blocks
- Convergence blocks
- Computational sequence
- Output format

At this stage the input process is complete and the ASPEN has prepared an input file from the graphical input procedure.

Execution

1. An Input translator reads the user input and generates a FORTRAN main program for execution. It sets up the data structures and generates computing sequence of equipment modes.
2. The program is compiled by a FORTRAN compiler.
3. A Linkage editor loads the simulation engine and links the program to the User defined and ASPEN libraries.
4. All the data supplied by user input and ASPEN related to the problem is stored in the problem data file.
5. Simulation is run and the related data is supplied by the problem data files. The simulation results are stored in the problem data files.
6. Report writer accesses the problem data files and writes the report in the format defined by the user.

The flow of information in the AspenPlus is shown in figure 5.1.

5.2 Simulation Procedure

The simulation procedure involves two steps

I. *Calculation of Thermodynamic Properties*

- Calculation of ΔG of all the reactions
- Calculation of K_P for all the reactions

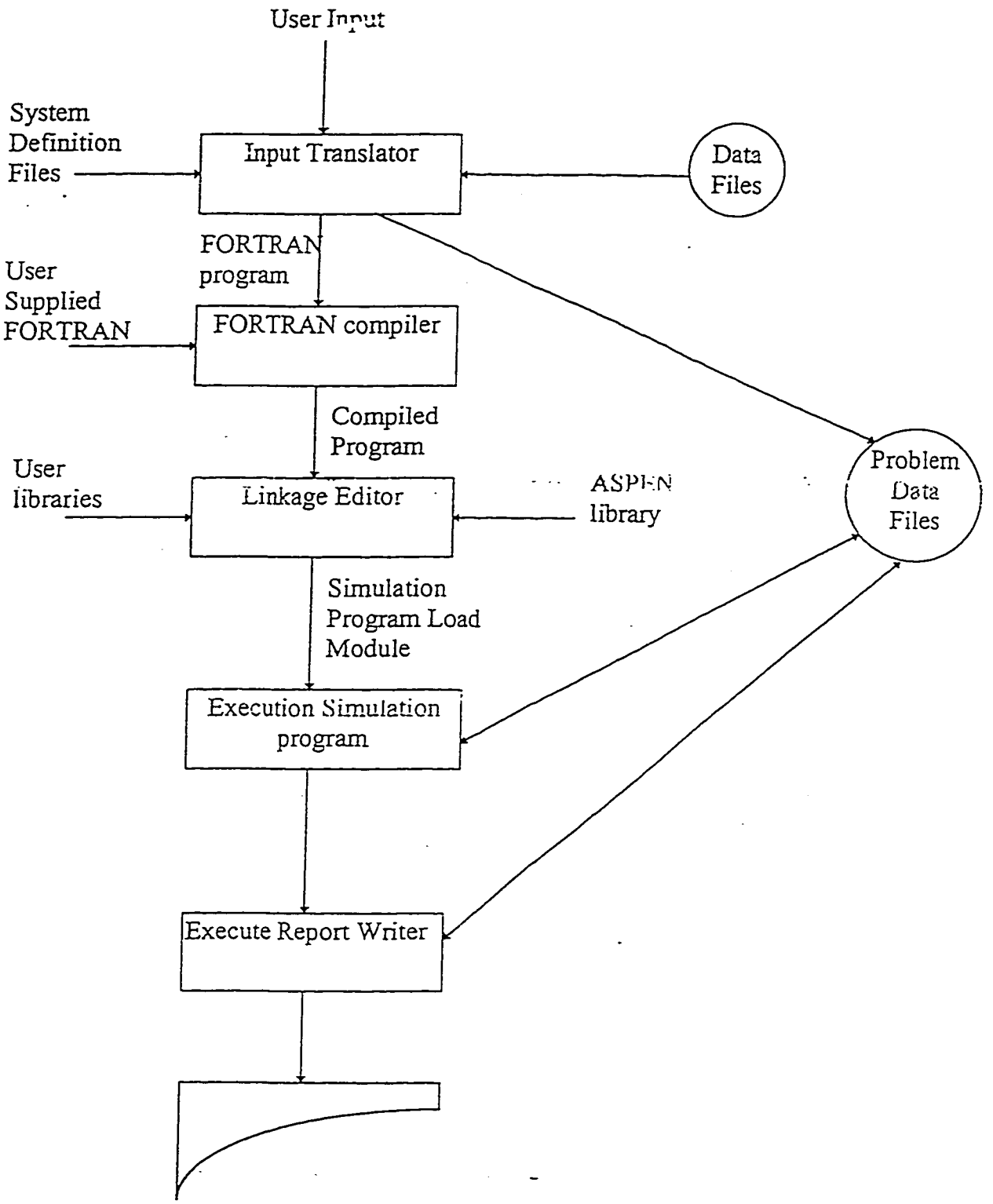


Figure 5.1 The flow of information in the AspenPlus

- Calculation of enthalpy of all the components
- Calculation of the heat of the reactions of all the reactions

II. *Simulation of the system of the reactions*

The reactions are either simulated

A. By AspenPlus

B. By FORTRAN code.

I. *Calculation of Thermodynamic Properties*

- **Standard Gibbs free energy of formation $\Delta G_{f_i}^{\circ}$**

Standard Gibbs free energy of formation at temperature T_o is the change in Gibbs free energy when one lb-mole of the compound is formed from its elements with all species in their standard states at T_o.

- **Standard Gibbs free energy of reaction ΔG_R°**

Standard Gibbs free energy of reaction at temperature T_o is the change in Gibbs free energy when the reaction takes place with all the reactants in their standard states at T_o. It can be obtained from the standard Gibbs energy of formation and the stoichiometry of the reaction as follows :

$$\Delta G_R^{\circ} = \sum_{i=1}^{n} \nu_i \Delta G_{f_i}^{\circ}$$

ν_i = Stoichiometric coefficients

$\Delta G_{f_i}^{\circ}$ = Gibbs free energy of formation of individual components

- **Equilibrium constant of a reaction**

Equilibrium constant of a reaction is the ratio of the ratio of the rate of the forward reaction to the rate of the backward reaction. It is obtained from the Gibbs free energy of the reaction as follows :

$$\Delta G_R^{\circ} = - RT \ln K_P$$

$$K_P = \text{Exp} \left\{ - \frac{\Delta G_R^{\circ}}{RT} \right\}$$

R = universal gas constant

T = temperature

- **Standard Enthalpy of formation ΔH_f°**

Standard enthalpy of formation at temperature T is the enthalpy when one lb-mole of the compound is formed from its elements with all species in their standard states at T_o.

- **Enthalpy of the compounds**

Enthalpy of a compound at temperature T is the heat content of the compound with reference to standard temperature. It can be obtained from the standard enthalpy of the formation of the compound as follows :

$$H_i^{\circ} = \Delta H_f^{\circ} + \left(H^{\circ} - H_{298}^{\circ} \right)_T$$

ΔH_f° = enthalpy of formation

$\left(H^\circ - H_{298}^\circ\right)_T$ = heat content at temperature T ^{0}K

- **Standard enthalpy of the reaction ΔH_R°**

Standard enthalpy of reaction at temperature T_o is the change in enthalpy when the reaction takes place with all the reactants in their standard states at T_o. It can be obtained from the standard enthalpy of formation and the stoichiometry of the reaction as follows :

$$\Delta H_R^\circ = \sum_{i=1}^{n} \nu_i H_i^\circ$$

ν_i = stoichiometric coefficients

H_i° = enthalpy of individual components

II. Simulation of the system of the reactions

A. Simulation on ASPENPlus

These reactions can be classified into two categories as shown in the Figure 3.1. Reactions 3.1 & 3.2 are primary reactions. These reactions go to completion as it is evident from their equilibrium constants presented in Table 6.1. Hence, the conversion for reactions 3.1 & 3.2 is 100% and limiting reactant for reactions 3.1 & 3.2 is oxygen. Secondary reactions (3.3 & 3.4) do not go completion, as it is evident from the equilibrium constants of these reactions (3.3 & 3.4), which are small as shown in figure

to the far right (Eastman 1956). Experimental work carried out by Eastman in 1956 has shown that free oxygen is not a component of the product and the partial oxidation is characterized by presence of carbon monoxide and hydrogen with carbon dioxide and water vapor in very small traces.

The combustion chamber is simulated into two reaction zones as shown in chapter 3. Exothermic reactions 3.1 and 3.2 take place in the first stage. These reactions are simulated by using RSTOIC in ASPENPlus. Endothermic reactions 3.3, 3.4 and 3.5 take place in second stage. These reactions are simulated by using REQUIL in ASPENPlus.
The system under investigation is simulated as shown in Figure 5.1, where :

Equipment B1: Combustion chamber

Stream 1: sour natural gas (INPUT)

Stream 2: Oxidant (INPUT)

Stream 3: Synthesis gas (OUTPUT)

The exothermic reactions 3.1and 3.2 have large equilibrium constants, which indicate that these reactions go to completion. Hence, the conversion of the reaction are known. So, primary reactions are simulated by RSTOIC. The endothermic reactions 3.3 to 3.5 have small equilibrium constants. Hence, the conversion of the reactions are not known. So, secondary reactions are simulated by REQUIL.

INPUT TO ASPENPLUS

Feed Flow Rate

Feed Composition

Feed Temperature

Feed Pressure

Reactions (3.1 ,3.2)

Extent / Conversion of Reactions (3.1 ,3.2)

Limiting Reactants for Reactions (3.1 ,3.2)

Reactions (3.3 ,3.4 & 3.5)

Combustion chamber Temperature

Combustion chamber Pressure

B. Mathematical Model

Development of the following balances

- Mass Balance
- Heat / Enthalpy Balance
- Equilibrium Relationships

Mole fraction of methane in products = x_1

Mole fraction of carbon dioxide in products = x_2

Mole fraction of water vapor in products = x_3

Mole fraction of carbon monoxide in products = x_4

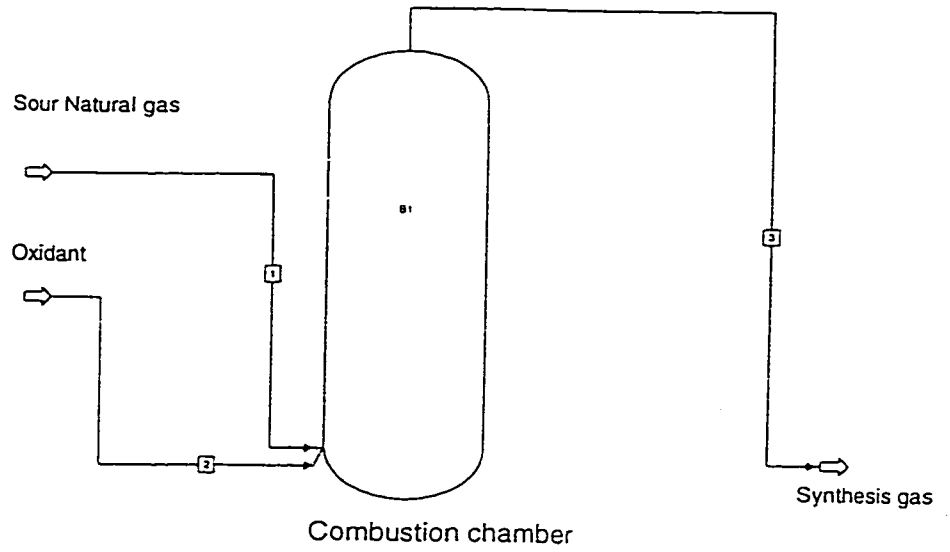


Figure 5.2 Simulation of combustion chamber for partial oxidation of sour natural gas

Mole fraction of hydrogen products = x_5

Mole fraction of sulfur dioxide in products = x_6

Moles of oxygen in feed per mole of methane in feed = x_7

Moles of hydrogen sulfide in feed per mole of methane in feed = x_8

Total moles of products per mole of methane in feed = x_9

Combustion chamber Temperature = T_R

Preheat Temperature = T_P

- **Mass Balances**

1. Oxygen

$$x_7 = (2x_2 + x_3 + x_4 + 2 x_6) x_9$$

2. Hydrogen

$$4+2 x_8 = (4 x_1 + 2 x_3 + 2 x_5) x_9$$

3. Carbon

$$1 = (x_1 + x_2 + x_4) x_9$$

4. Sulfur balance

$$1 = (x_6) x_9$$

5. Mole Faction Constraint

$$x_1 + x_2 + x_3 + x_4 + x_5 + x_6 = 1$$

- **Heat / Enthalpy Balance**

$$\left(H_{CH_4} + x_7 H_{O_2} + x_8 H_{H_2S}\right)_{T_P} = \begin{pmatrix} x_1 H_{CH_4} + x_2 H_{CO_2} + x_3 H_{H_2O} + \\ x_4 H_{CO} + x_5 H_{H_2} + x_6 H_{SO_2} \end{pmatrix} x_9$$

Equilibrium Relationships

1. $$K_2 = \frac{x_4^{\,2} x_5^{\,2} P^2}{x_1 x_2}$$

2. $$K_3 = \frac{x_5^{\,3} x_4 P^2}{x_1 x_3}$$

3. $$K_4 = \frac{x_5 x_2}{x_4 x_3}$$

Solution of the equations

Newton-Raphson technique was used for solution of system of non-linear algebraic equations. IMSL subroutine NEQNF was ussed to solve the system of non-linear algebraic equations (Appendices).

5.3 Absorption of Sulfur Dioxide

1. Water is used to absorb the SO_2 in a packed tower. A weak sulfurous acid is produced.
2. Extra SO_2 is supplied from the elementary sulfur to bring the sulfurous acid concentration to the concentration required for the modified Westinghouse process.

A weak aqueous solution of SO_2 and water (sulfurous acid) is produced which is concentrated by absorbing SO_2 produced from the oxidation of the elemental sulfur. The

concentration of the SO_2 in the water is brought to requirement of the modified Westinghouse process.

5.4 Open Sulfur-Cycle Process

This is a open cycle electrochemical system also known as Westinghouse process. Since the supply of the SO_2 is continuous, it is more beneficial to use open sulfur-cycle instead of closed sulfur-cycle. Open sulfur-cycle is similar to closed sulfur-cycle except that decomposition of H_2SO_4 is eliminated. Hydrogen is produced in a low temperature electrochemical step, wherein sulfuric acid and hydrogen is produced from sulfurous acid, i.e.,

$$2H_2O\,(l) + SO_2\,(aq) \rightarrow H_2SO_4\,(aq) + H_2\,(g) \qquad 298K\ (0.17V)$$

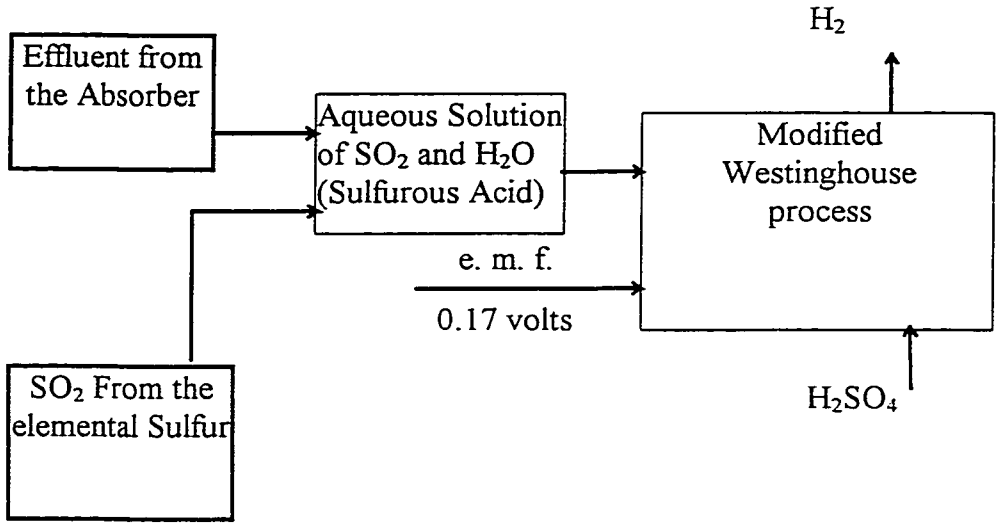
The open sulfur-cycle continuously produces sulfuric acid as a main product. The produced sulfuric acid has to be concentrated using multi-staged flashing before it is sold as a concentrated acid.

Hydrogen is generated electrolytically in an electrolysis cell which anodically oxidizes sulfurous acid to sulfuric acid while simultaneously generating hydrogen at the cathode.

Basis : 100 lb-mole/h of combustion chamber effluent

Combustion chamber effluent = 5 lb-mole of SO_2 , 95 lb-mole of synthesis gas

(Further details in chapter 6 page number 145)



Aqueous Solution of SO_2 and Water fed $L_2 = 3032832.282 \ \frac{lb_m}{h}$

Hydrogen produced from the modified Westinghouse process = $61239.88 \ \frac{lb_m}{h}$

Sulfuric acid produced = $2974508.31 \ \frac{lb_m}{h}$

CHAPTER 6

RESULTS AND DISCUSSION

In this chapter, results of simulation of the non catalytic partial oxidation process (NCPO) of sour natural gas is reported first in part A. The effect of the parameters like ratio of the moles of the oxygen in feed to the number of moles of methane in feed (molar equivalence ratio), hydrogen sulfide content in feed, heavier hydrocarbons (ethane and propane) in feed, preheat temperature and pressure on the hydrogen, carbon monoxide and sulfur dioxide production and ratio of sum of the moles of hydrogen and carbon monoxide in the product (carbon efficiency) and ratio of sum of moles of hydrogen and carbon monoxide in the product (oxygen efficiency) is discussed.

The results obtained by simulation of NCPO on AspenPlus are compared with simulation of NCPO by mathematical model. The results of simulation of NCPO by mathematical model as well as AspenPlus are compared with the results of Mungen and Kratzer for a feed of sweet natural gas. The simulation results obtained from AspenPlus is compared with the plant data of a petrochemical plant (Ibn Sina). Calculated values of the waste heat recovery are absorption system follows in the part B of the chapter. The feed is limited to hydrogen sulfide content of 0, 3, 5, 7, or 10 % and ethane to 5 mole% and propane to 5 mole% for the hydrocarbons heavier than methane.

Part A. Simulation of the NCPO process

6.1 Calculation of Thermodynamic Properties

In the simulation, it was necessary to carry out first some basic calculation of the thermodynamic properties including:

- Calculation of Gibbs energy of reaction of all the reactions
- Calculation of equilibrium constant of all the reactions
- Calculation of enthalpy of all the components
- Calculation of the heat of the reactions of all the reactions

These calculations were carried out for different reactions and the results are tabulated in the Tables 6.1, and 6.2.

Table 6.1 Basic Reactions With Thermodynamic Data

#	Reactions	ΔH Kcal/mol		ΔG Kcal/mol		ln K_P		K_P*	
		1700F	2200F	1700F	2200F	1700F	2200F	1700F	2200F
3.1	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-191.2	-192.2	-191.31	-191.2	80.234	65.12	7 E34	1.92E28
3.2	$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O$	-124.6	-124.5	-101.5	-96.2	42.57	32.77	3.07E18	1.7E14
3.3	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	196.253	137.778	-19.304	-38.092	8.096	12.974	3.28E3	4.3E5
3.4	$CH_4 + H_2O \rightarrow CO + 3H_2$	119.093	121.809	-18.365	-35.439	7.702	12.07	2.2E3	1.75E5
3.5	$CO + H_2O \leftrightarrow H_2 + CO_2$	-64.8	-65.4	-0.739	-2.653	0.31	0.9036	1.363	2.468

* Units for K_P

- Reaction 3.1 [-]
- Reaction 3.2 [$atm^{-0.5}$]
- Reaction 3.3 [atm^2]
- Reaction 3.4 [atm^2]
- Reaction 3.5 [-]

Table 6.2 Calculation of Thermodynamic Properties *

	ΔG_f^0		$H^0-H^0_{298}$		ΔH_f^0		ΔH	
	1700 F	2200 F	1700 F	2200 F	1700 F	2200 F	1700 F	2200 F
CH_4	9.887	17.262	12.732	18.22	-21.854	-22.092	30.952	-3.634
H_2O	-43.371	-39.366	8.24	11.246	-59.519	-59.804	19.486	-48.273
CO_2	-94.681	-94.727	10.632	14.44	-94.419	-94.548	25.072	-79.979
CO	-52.049	-57.781	6.794	9.097	-27.062	-27.5	15.891	-17.965
H_2	0	0	6.404	8.496	0	0	14.9	8.496
O_2	0	0	7.14	9.511	0	0	16.651	9.511
S	34.881	30.865	4.77	6.179	52.155	52.325	10.949	58.334
SO_2	-65.582	-60.757	10.866	14.611	-86.49	-86.382	25.477	-71.879
H_2S	-7.49	-4.213	8.934	12.258	-21.636	-21.652	21.192	-9.378

* Units are given in Table 6.1

6.2 Hydrogen Production

The production of the hydrogen depends upon a number of parameters. Hydrogen is formed in the second stage when carbon dioxide and steam reacts with unreacted methane. Hence, number of moles of hydrogen depends upon the amount of carbon dioxide and steam produced and methane left unreacted in the first stage. All of these depend upon the amount of oxygen fed per mole of methane. The number of moles of hydrogen also depends on the preheat temperature, hydrogen sulfide content of feed, pressure and heavier hydrocarbons like ethane and propane in the feed.

6.2.1 Effect of equivalence ratio

The equivalence ratio is the most important independent variable in the non-catalytic partial oxidation process and has direct effect on the reaction temperature. The equivalence ratio is the ratio of the number of moles of the oxygen in the feed to the number of moles of the natural gas in the feed. In order to raise the temperature for a higher conversion of methane, the oxygen concentration in the feed must be increased so that more heat is released by methane reacting with the oxygen. It is very important that a suitable amount of heat be supplied by a reasonable methane to oxygen ratio in order to reach a suitably high combustion chamber temperature for the partial oxidation reactions to take place. A deficiency in oxygen results in carbon formation, while excess oxygen consumes the greater amount of raw material per unit of synthesis gas and increases the production of carbon dioxide and steam at the expense of hydrogen and carbon monoxide [Latta and Walter,1948]. The effect of equivalence ratio on the numbers of

moles of hydrogen is shown in Figure 6.1. There is indication of large change in the concentration of hydrogen with increasing equivalence ratio. The concentration of hydrogen increases with increasing equivalence ratio and reaches a maximum value at optimum equivalence ratio. This maximum occurs at ER = 0.525 for a feed of 95% methane and 5% H_2S.

At lower equivalence ratios, the amount of oxygen supplied is low, so a small amount of methane reacts with this oxygen to form low amounts of steam and carbon dioxide which reacts with the methane in secondary reactions 3.3 and 3.4 and produces low amount of hydrogen. So, initially no steam and carbon dioxide appears in the product. Only small amount of hydrogen appears in the product along with large amount of unreacted methane.

At equivalence ratio in vicinity of one-half, the oxygen is supplied in stoichiometric amount for the partial oxidation. So, the primary reactions 3.1 and 3.2 produces sufficient steam and carbon dioxide to consume all of the unreacted methane in the secondary reactions 3.3 and 3.4. Thus, no unreacted methane appears in the product and complete conversion is achieved at this equivalence ratio. The region marked by zero equivalence ratio and 0.525 equivalence ratio for a feed with 5% H_2S, is the region of partial oxidation.

At equivalence ratio higher than 0.525, the oxygen supplied is more than sufficient for

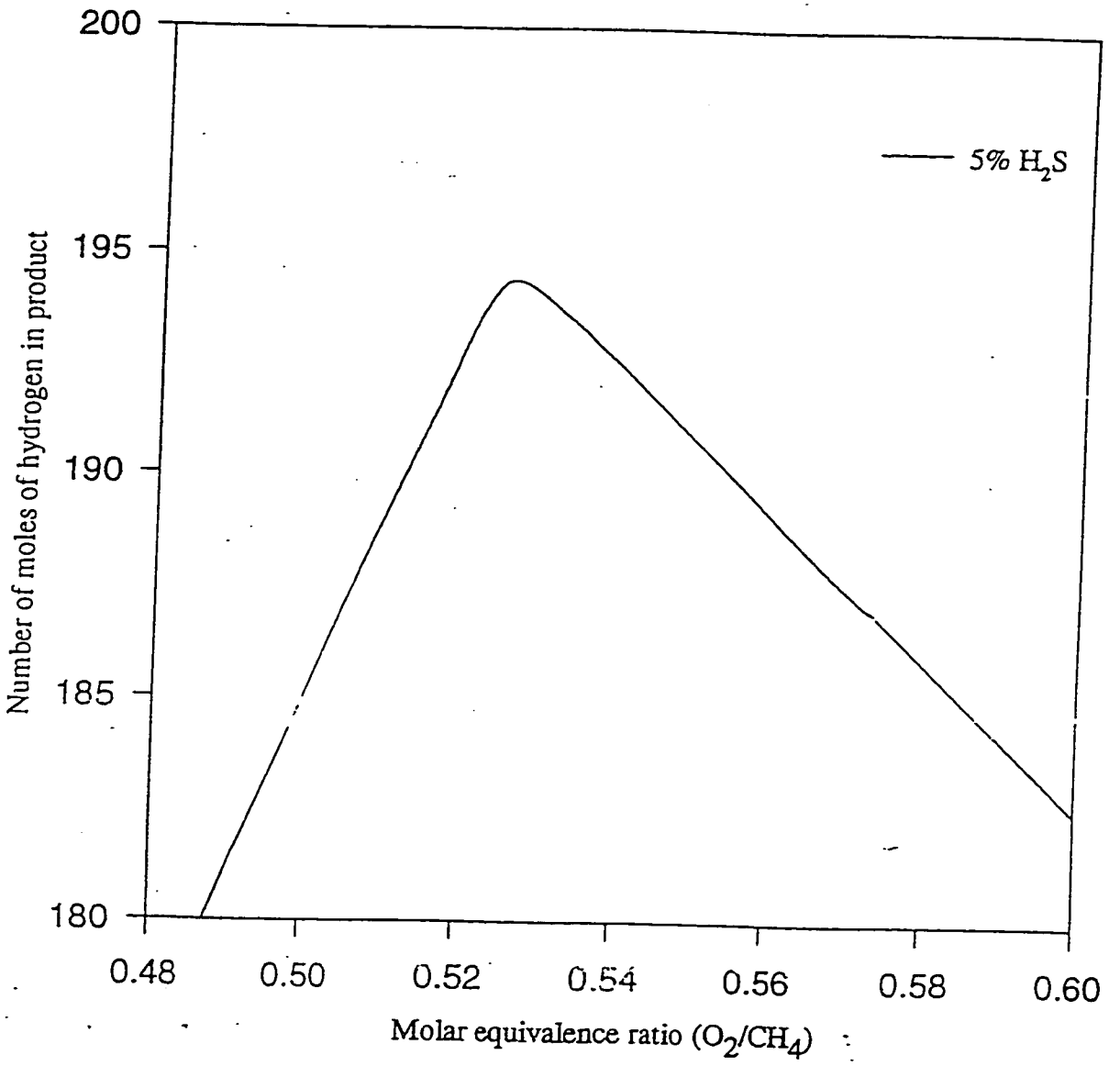


Figure 6.1 Variation of number of moles of H_2 in the product with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 48-60

partial oxidation. So, the primary reactions 3.1 and 3.2 produce more steam and carbon dioxide than required for partial oxidation at the expense of methane. More oxygen consumes more amount of methane. So, lower amount of methane is available to secondary reactions 3.3 to 3.4. Hence, as a result surplus steam and carbon dioxide appears in the product. This affects the production of hydrogen. It drops till the equivalence ratio of two, where it becomes zero. At this equivalence ratio, all of the methane is consumed by the primary reactions 3.1 and 3.2 and secondary reactions do not take place.

6.2.2 Effect of the hydrogen sulfide content of feed

The content of hydrogen sulfide in the sour natural gas has direct effect on the number of moles of hydrogen. The number of moles of hydrogen decrease with the increase in the hydrogen sulfide content of the sour natural gas as shown in the Figure 6.2. The partial oxidation of the hydrogen sulfide is highly exothermic. There is a gradual shift in the optimum equivalence ratio with increase in the hydrogen sulfide content of the sour natural gas. This is due to the fact that hydrogen sulfide requires 1.5 times oxygen than that required by the methane.

The partial oxidation of the hydrogen sulfide does not produce any hydrogen whereas methane and other hydrocarbons produce hydrogen upon partial oxidation. So, there is a decrease in the hydrogen production with the increase in the hydrogen sulfide content of the feed.

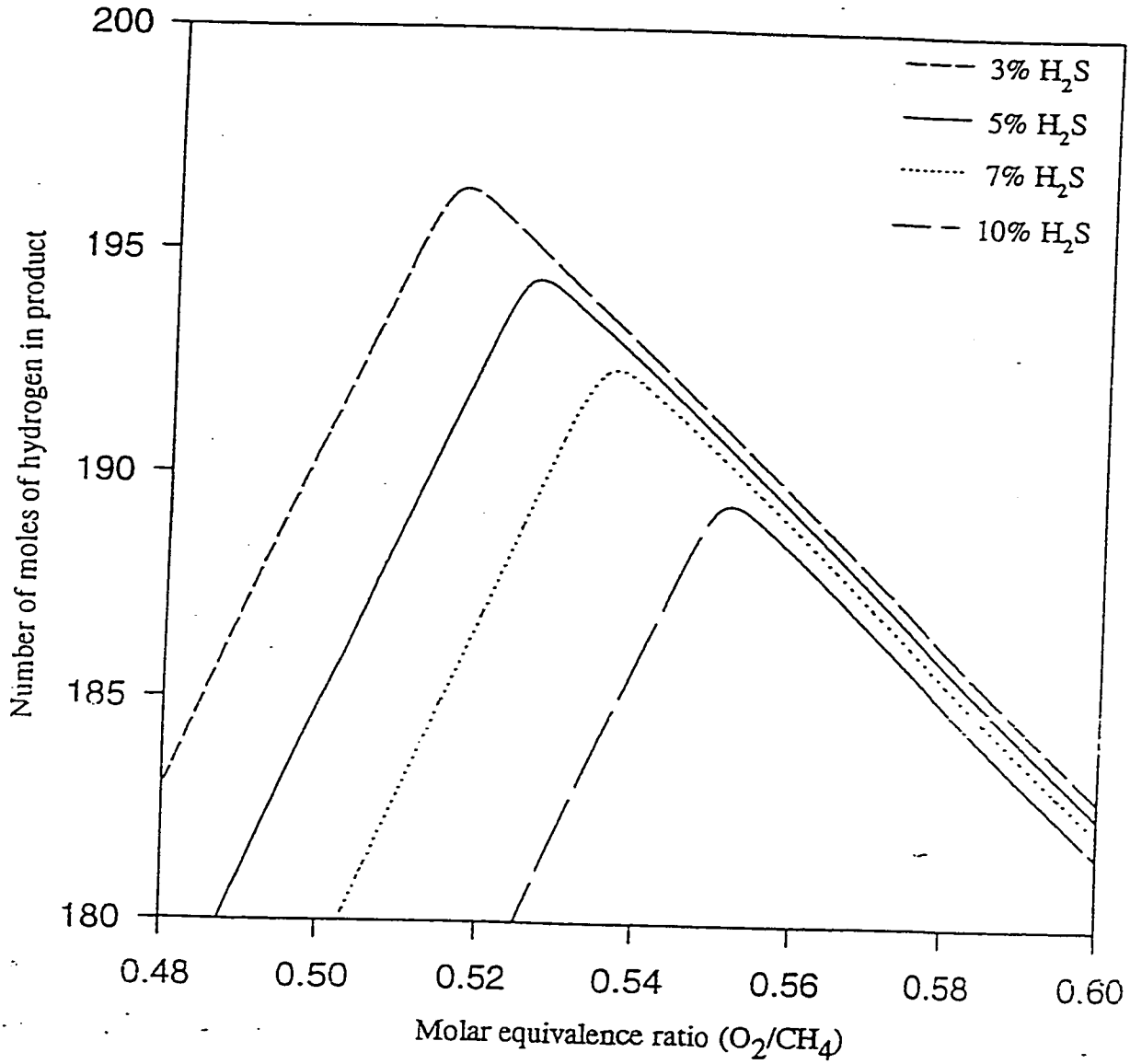


Figure 6.2 Effect of H_2S content on the number of moles of H_2 in the product

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 90-97, moles H_2S 10-3, moles O_2 48-60

6.2.3 Effect of heavier hydrocarbons in the feed

The number of moles of the hydrogen increases with the increases in the content of the heavier hydrocarbons in the feed as shown in the Figure 6.3. Methane contains largest number of hydrogen atoms per atom of carbon. The simulation was carried out with a 5 mole% ethane and 5 mole% propane in feed. Both contain less number of hydrogen atoms per atom of carbon than methane. The number of moles of hydrogen in product increase in content of heavier hydrocarbons in sour natural gas.

The sour natural gas is purchased on the basis of weight, the effect o the increase in the content of heavier hydrocarbons would be reversed.

6.2.4 Effect of preheat temperature

The number of moles of hydrogen is lower for lower preheat temperature of natural gas as shown in the Figure 6.4. Higher preheat temperature results in high hydrocarbon conversion, as the higher temperature favor the endothermic secondary reactions. Preheat of oxygen also increases the number of moles of hydrogen. Prior to partial oxidation, sour natural gas and oxygen are preheated separately to avoid complete combustion, formation of carbon, explosion in preheater, side reactions, flame in supply pipes and to stay in safe limits of inflammability.

The preheat temperature is limited by two factors. First is the design of the pre heater, which should be such that there are no local hot spots or stagnant pockets where methane

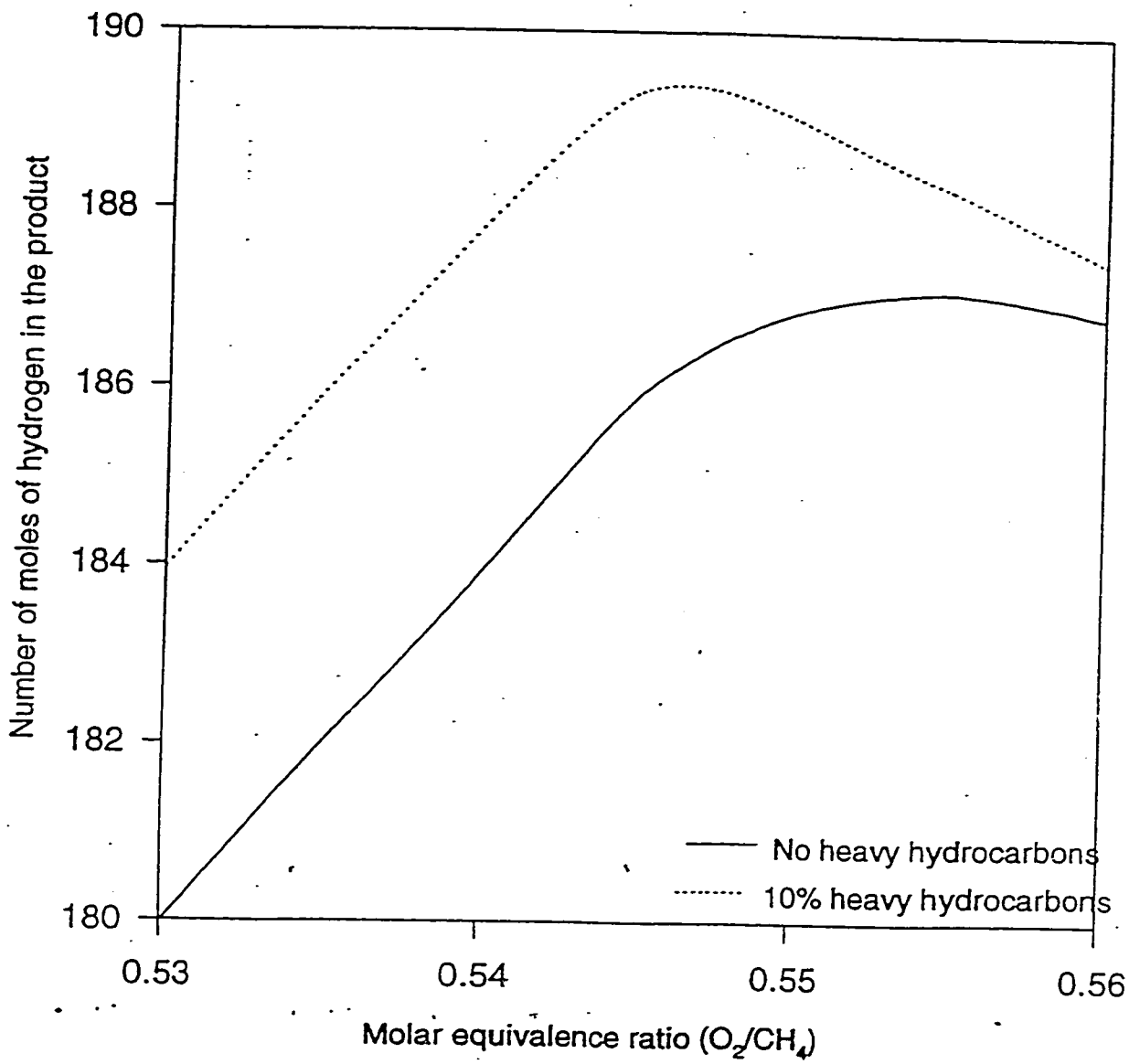


Figure 6.3 Effect of hydrocarbons heavier than methane on the number of moles of H_2 in the product

Operating Conditions

Pressure = 15 psi

Temperature = 2200 ^{0}F

Preheat Temperature = 1200 ^{0}F

Feed = moles CH_4 80-90, moles H_2S 10, moles O_2 52-57, moles C_2H_6 5-0, moles C_3H_8 5-0

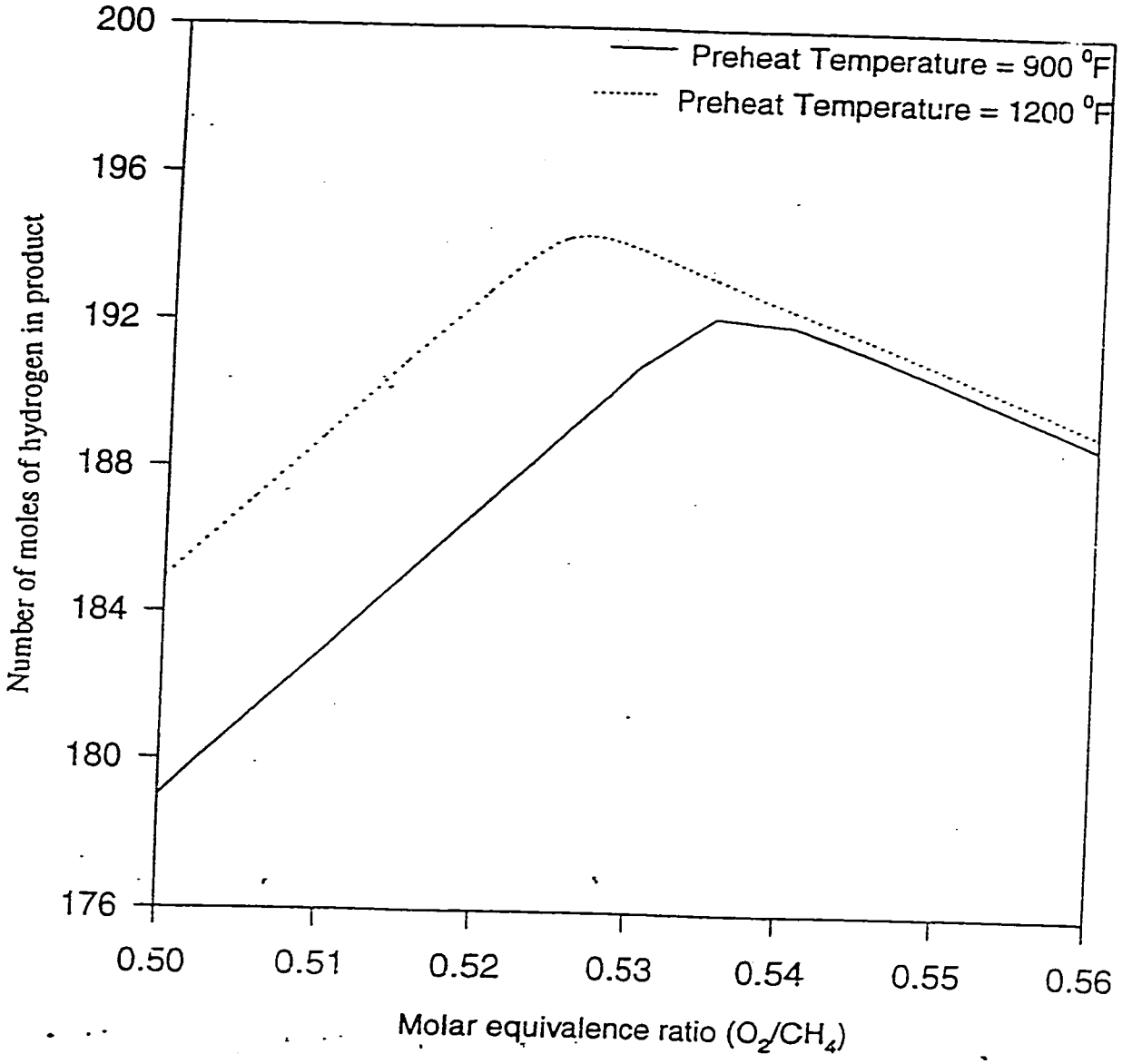


Figure 6.4 Effect of the preheat temperature on the number of moles of H_2 in the product

Operating Conditions
Temperature = 2200 °F
Pressure = 15 psi
Preheat Temperature = 1200 °F and 900 °F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 50-56

will decompose. The second is the temperature at which spontaneous ignition will occur

Figure 6.2 Effect of H_2S content on the number of moles of $H_2$when the oxidant and methane is premixed. Sour natural gas is not preheated above 1200 ^{0}F to avoid cracking and carbon deposition. Oxygen is very reactive above 1000 ^{0}F, so it is not preheated above 1000 ^{0}F.

6.2.5 Effect of pressure

Increase in the pressure lowers the number of moles of hydrogen as shown in the Figure 6.5. Increase in the pressure adversely affects the secondary reactions 3.3 and 3.4, resulting in the lower number of moles of hydrogen. The disadvantages of pressure operation lie in the adverse effect on equilibrium and the severe mechanical problems that will be introduced in this high temperature process.

6.3 Carbon Monoxide Production

The production of the carbon monoxide depends upon a number of parameters. Carbon monoxide is formed in the second stage when carbon dioxide and steam reacts with unreacted methane. The number of moles of carbon monoxide depends upon the amount of carbon dioxide and steam produced and methane left unreacted in the first stage. Similar to hydrogen production, the number of moles of carbon monoxide also depends on the same parameters described earlier, as shown in the Figures 6.6 to 6.10.

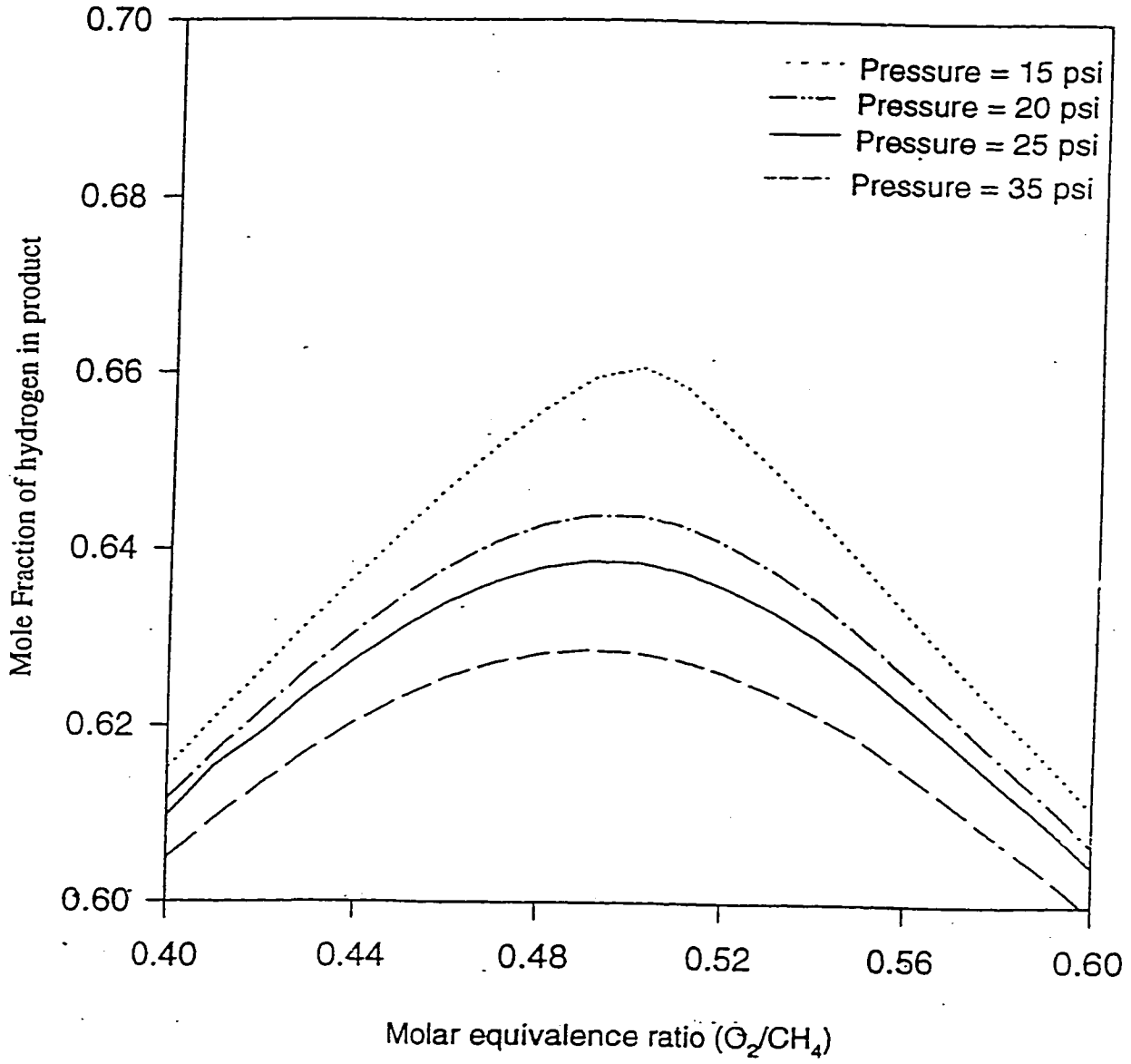


Figure 6.5 Effect of the pressure on the number of moles of H_2 in the product

Operating Conditions
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Pressure = 15psi, 20 psi, 25psi, 35psi
Feed = moles CH_4 100, moles O_2 40-60

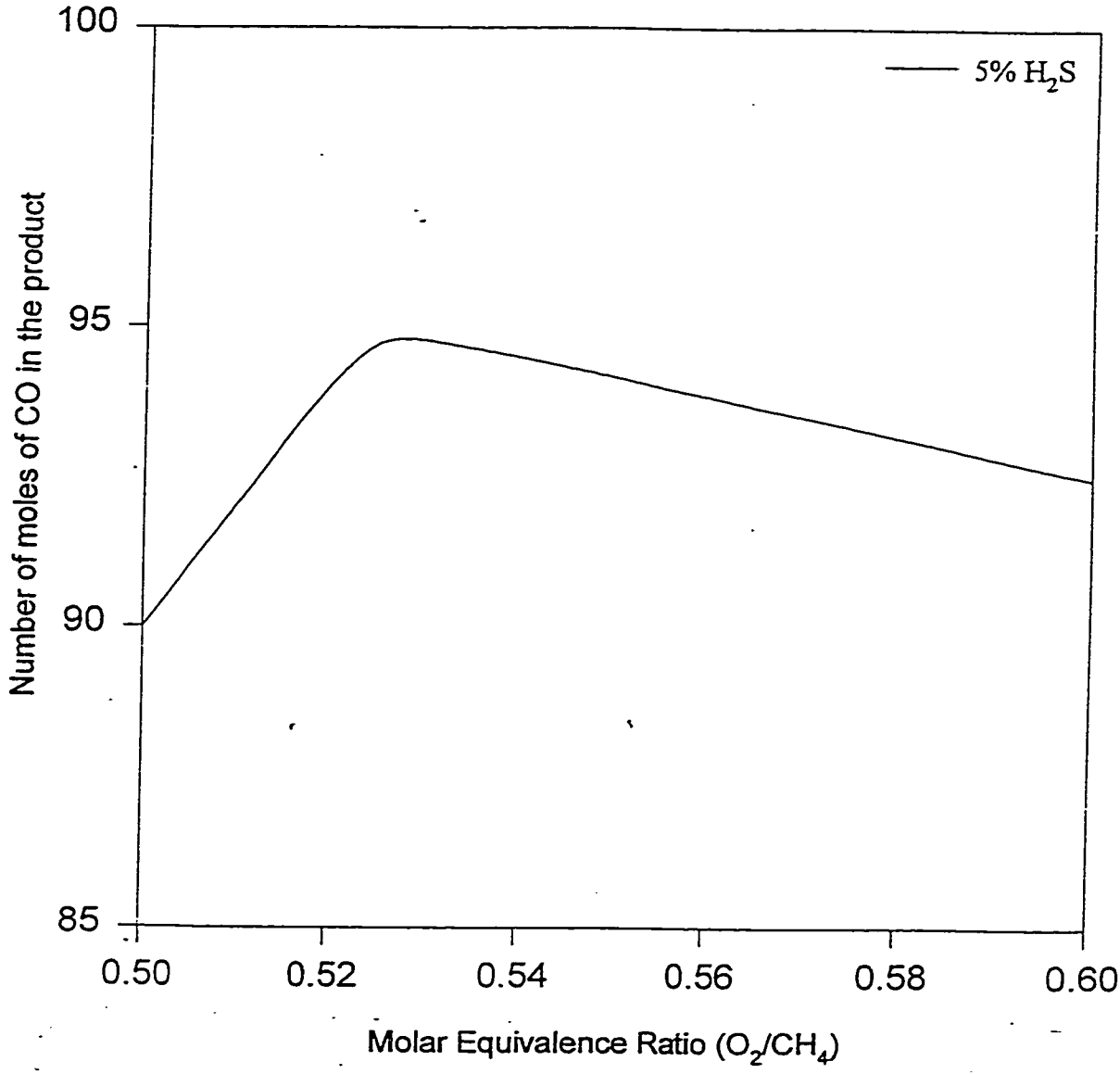


Figure 6.6 Variation of the number of moles of CO in the product with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 48-60

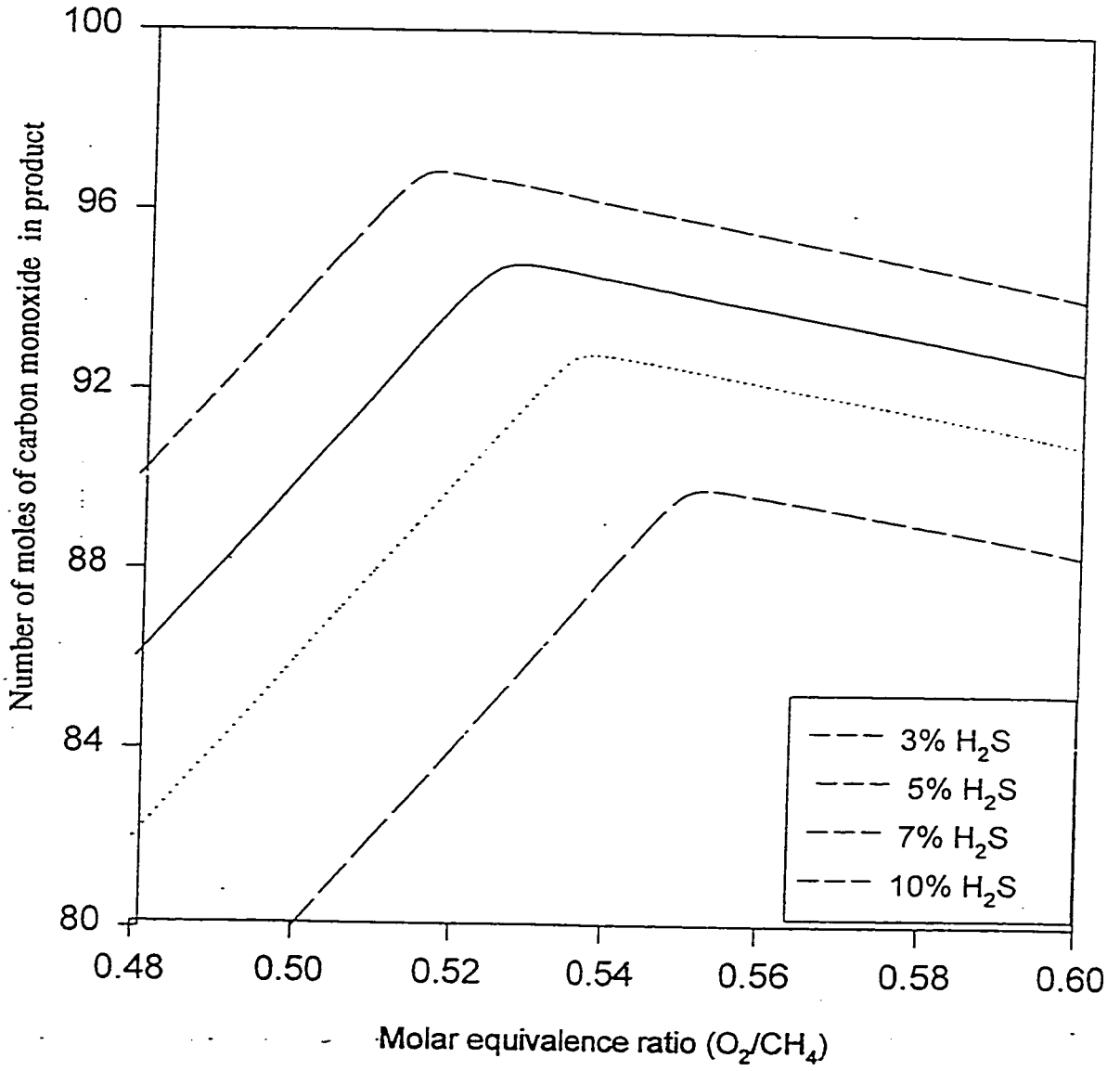


Figure 6.7 Effect of the H_2S content on the number of moles of the CO in the product

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 90-97, moles H_2S 10-3, moles O_2 48-60

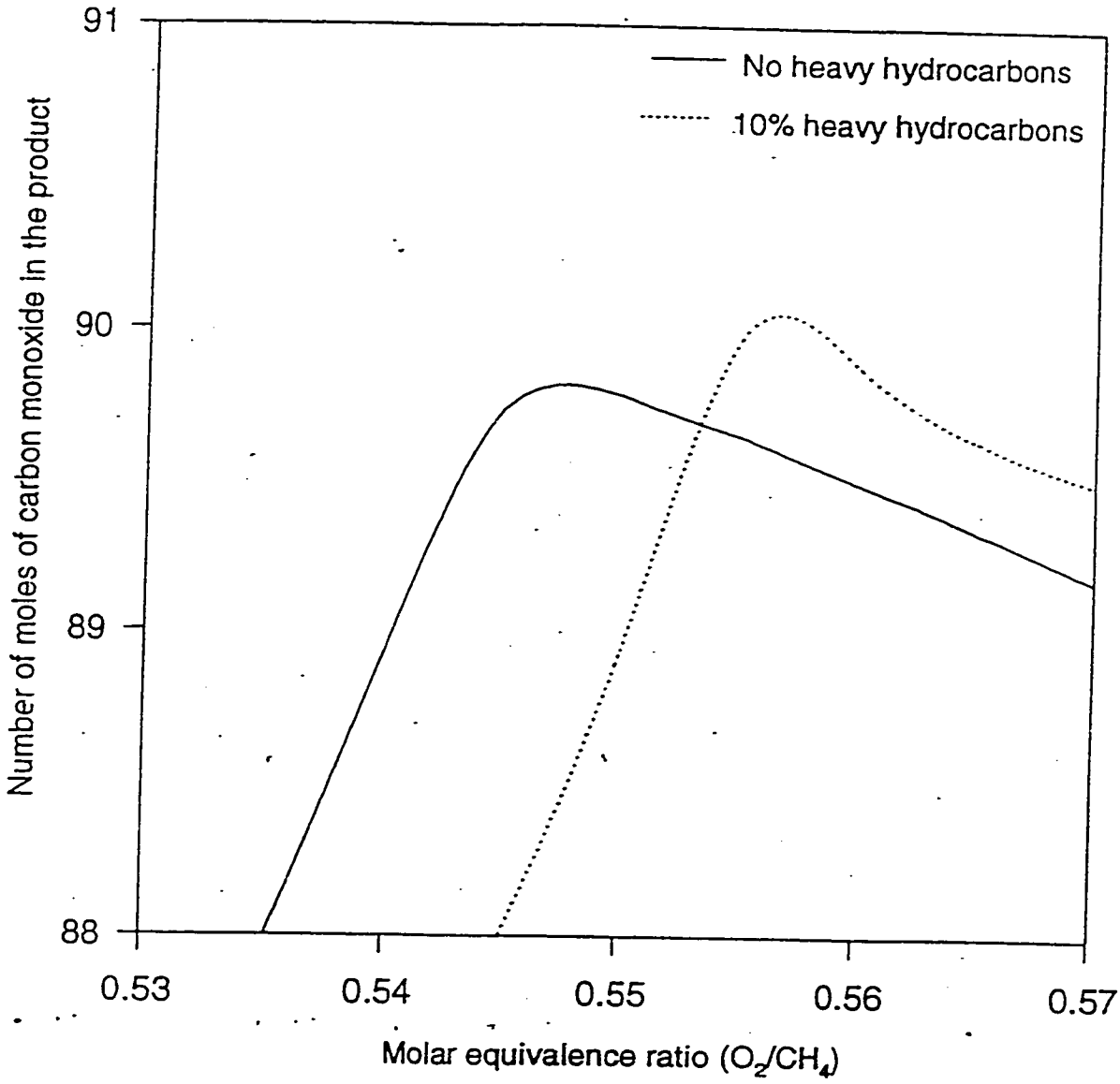


Figure 6.8 Effect of hydrocarbons heavier than methane on the number of moles of Co in the product

Operating Conditions

Pressure = 15 psi

Temperature = 2200 ^{0}F

Preheat Temperature = 1200 ^{0}F

Feed = moles CH_4 80-90, moles H_2S 10, moles O_2 52-57, moles C_2H_6 5-0, moles C_3H_8 5-0

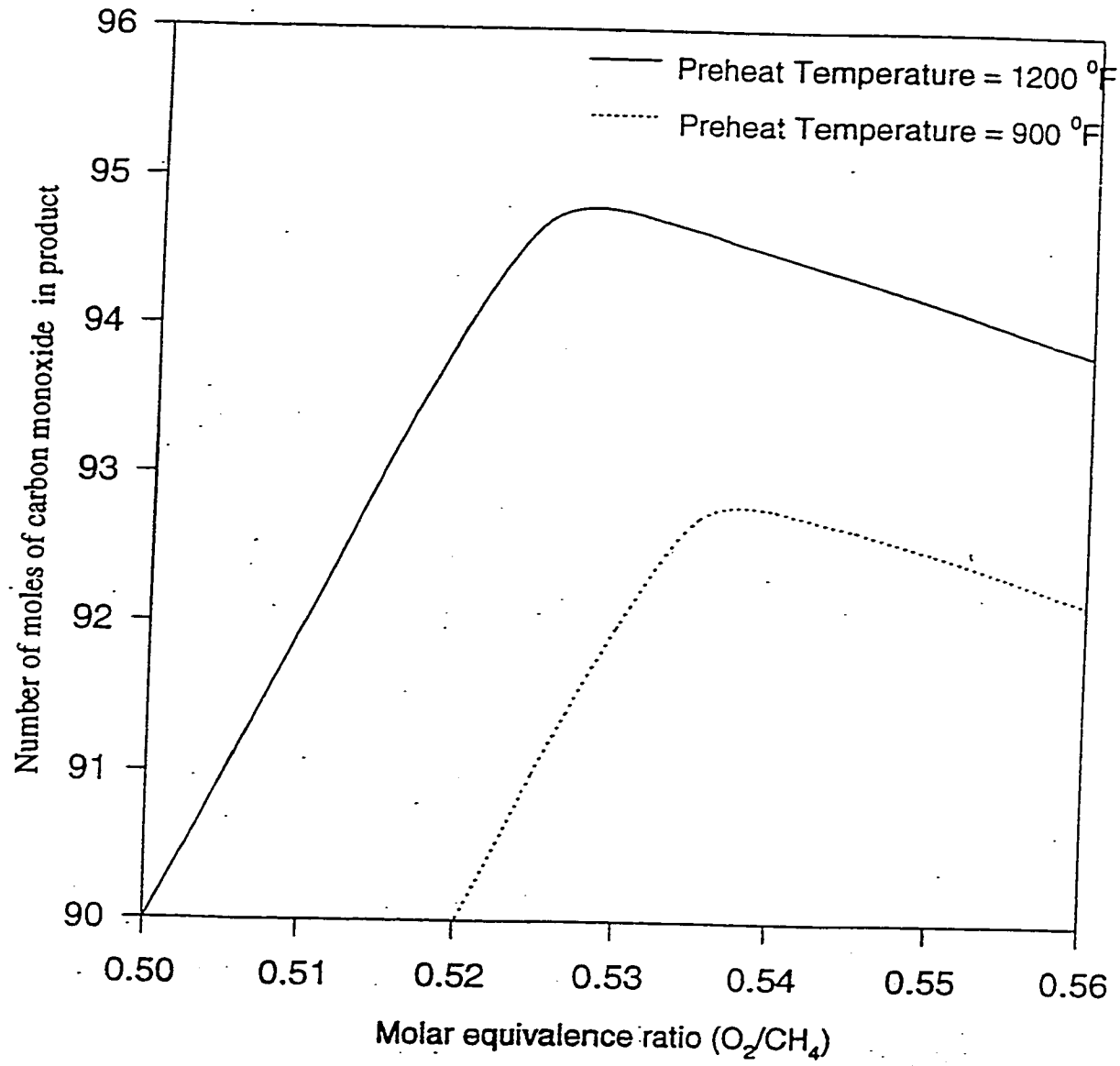


Figure 6.9 Effect of the preheat temperature on the number of moles of CO in the product

Operating Conditions
Temperature = 2200 °F
Pressure = 15 psi
Preheat Temperature = 1200 °F and 900 °F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 51-59

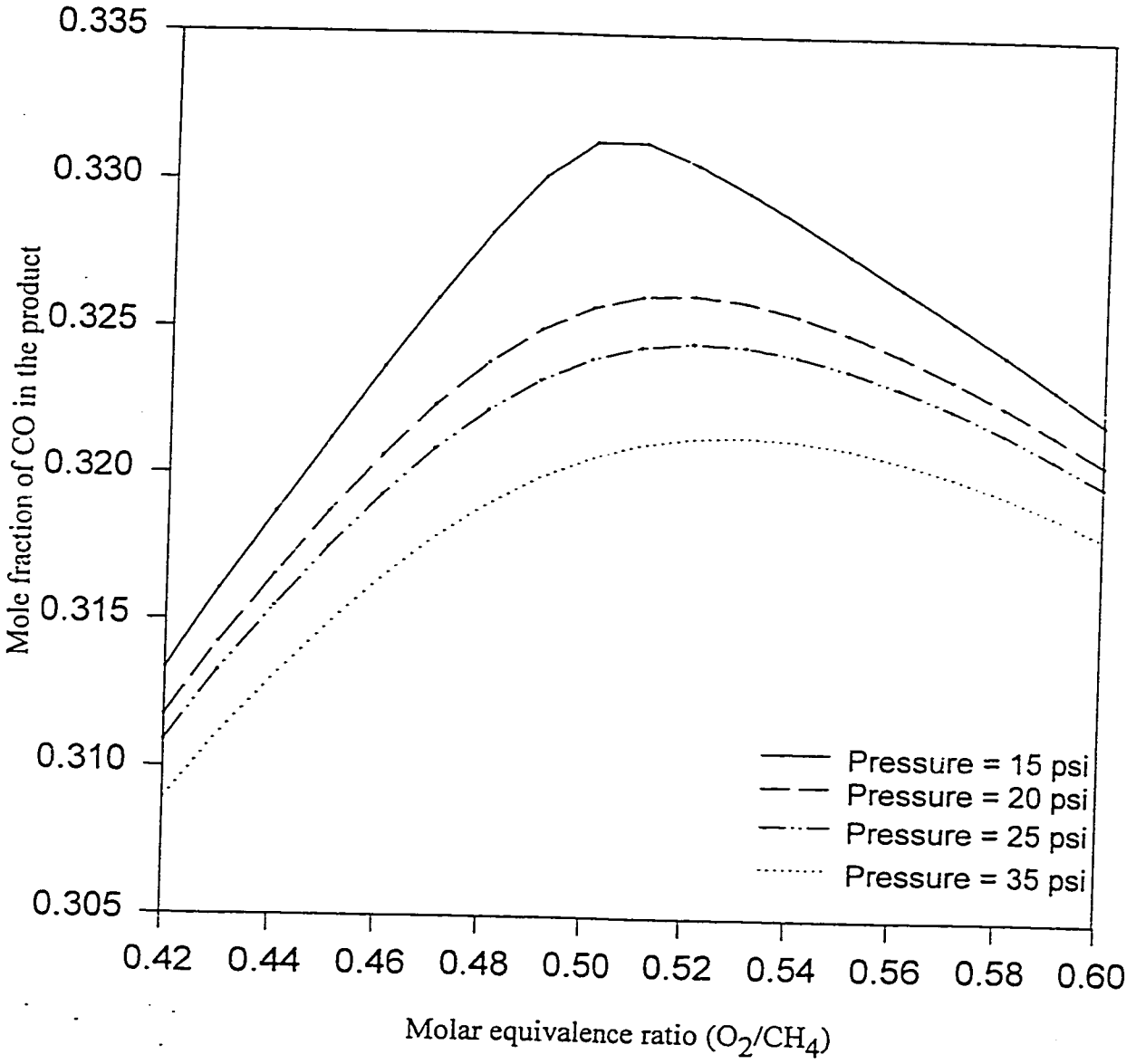


Figure 6.10 Effect of the pressure on the number of moles of CO in the product

Operating Conditions
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Pressure = 15psi, 20 psi, 25psi, 35psi
Feed = moles CH_4 100, moles O_2 42-60

the number of moles of sulfur dioxide depends upon the amount of oxygen fed per mole of methane. The number of moles of sulfur dioxide also depends on the preheat temperature, hydrogen sulfide content of feed, pressure and heavier hydrocarbons, like ethane and propane in the feed.

6.4.1 Effect of equivalence ratio (ER)

Effect of equivalence ratio on the number of moles of sulfur dioxide shows the same pattern. It increases initially then reaches a steady value as shown in Figure 6.11. This occurs at ER of 0.1. At lower equivalence ratios, the oxygen supplied is lower than required for the partial oxidation of the hydrogen sulfide. Hence, unreacted hydrogen sulfide appears in the product stream. At equivalence ratio of 0.1, sufficient oxygen is supplied for the partial oxidation of hydrogen sulfide. All of the hydrogen sulfide is converted in to sulfur dioxide, hence, no hydrogen sulfide appears in the product stream.

6.4.2 Effect of hydrogen sulfide content in feed

The hydrogen sulfide content in the sour natural gas has a direct effect on the number of moles of sulfur dioxide in the product. The number of moles of sulfur dioxide in the product increases with the increases in the hydrogen sulfide content of the sour natural gas as shown in Figure 6.12. The partial oxidation of the hydrogen sulfide results in sulfur dioxide and steam, whereas the methane is oxidized to hydrogen and carbon monoxide. There is a gradual shift in optimum equivalence ratio with an increase in hydrogen sulfide content of sour natural gas. This is because of the fact that larger amounts of hydrogen

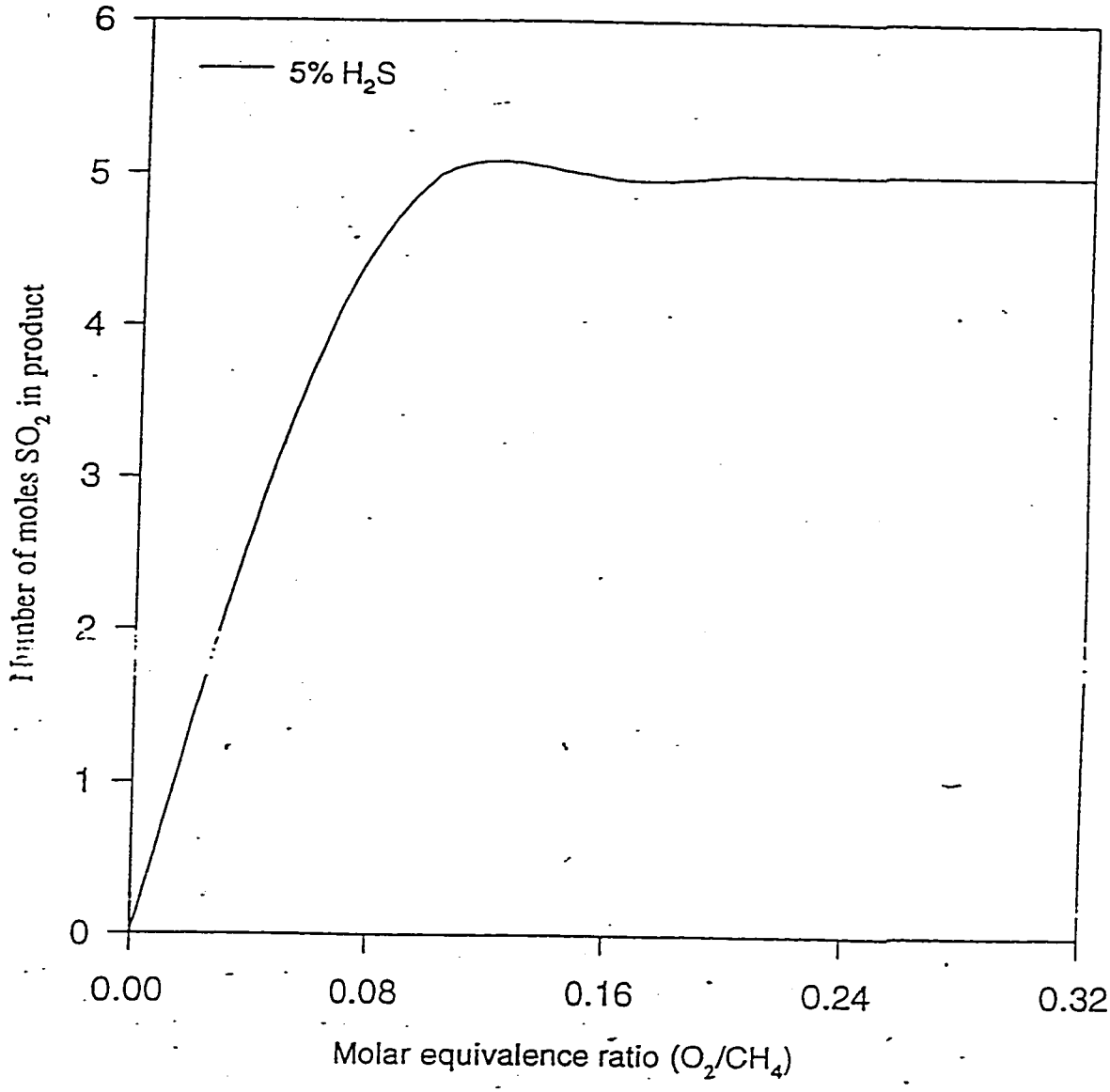


Figure 6.11 Variation of number of moles of SO_2 in the product with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 0-32

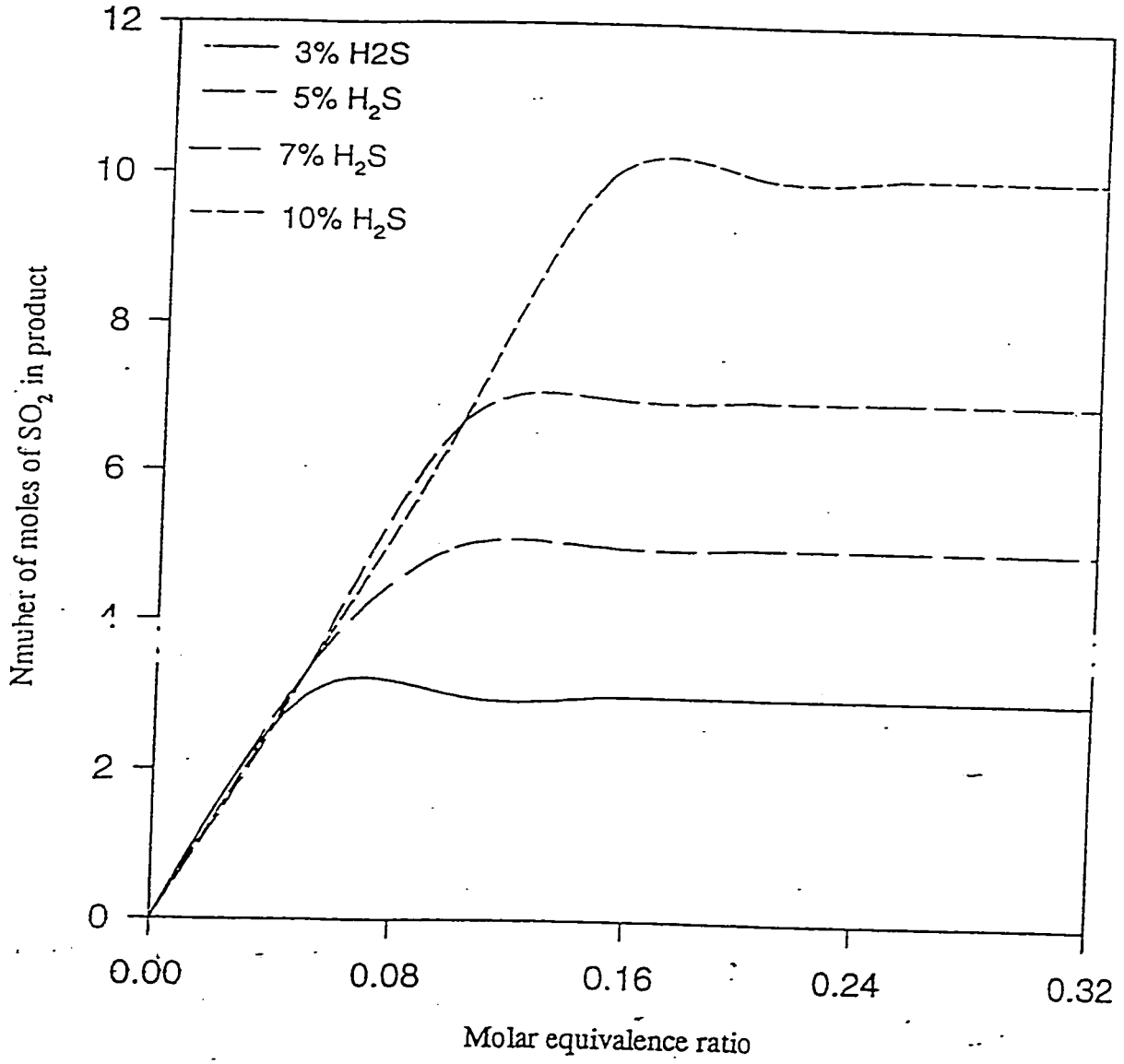


Figure 6.12 Effect of the H_2S content on the number of moles of SO_2 in the product

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 90-97, moles H_2S 10-3, moles O_2 0-32

sulfide require greater amounts of oxygen.

6.5 Carbon Efficiency

The carbon efficiency depends upon a number of parameters. Carbon efficiency is the ratio of the sum of the moles of the hydrogen and carbon monoxide in the product to the number of the moles of the carbon in the feed. It depends on the number of moles of the hydrogen and carbon monoxide in the product. Hydrogen and carbon monoxide are formed in the second stage when carbon dioxide and steam reacts with unreacted methane. Hence, the number of moles of hydrogen and carbon monoxide depend upon the amount of carbon dioxide and steam produced and methane left unreacted in the first stage. Both of these depend upon the amount of oxygen fed per mole of methane. The number of moles of hydrogen and carbon monoxide also depends on the preheat temperature, hydrogen sulfide content of feed, pressure and heavier hydrocarbons, like ethane and propane in the feed.

6.5.1 Effect of molar equivalence ratio

Effect of equivalence ratio on the carbon efficiency shows the same pattern as the number of moles of the hydrogen and carbon monoxide. It increases initially then reaches a maximum then decreases as shown in Figure 6.13. This maximum occurs at ER = 0.515. The reason for this behavior is the same as the reason for the variation of the number of moles of the hydrogen and carbon monoxide in the product.

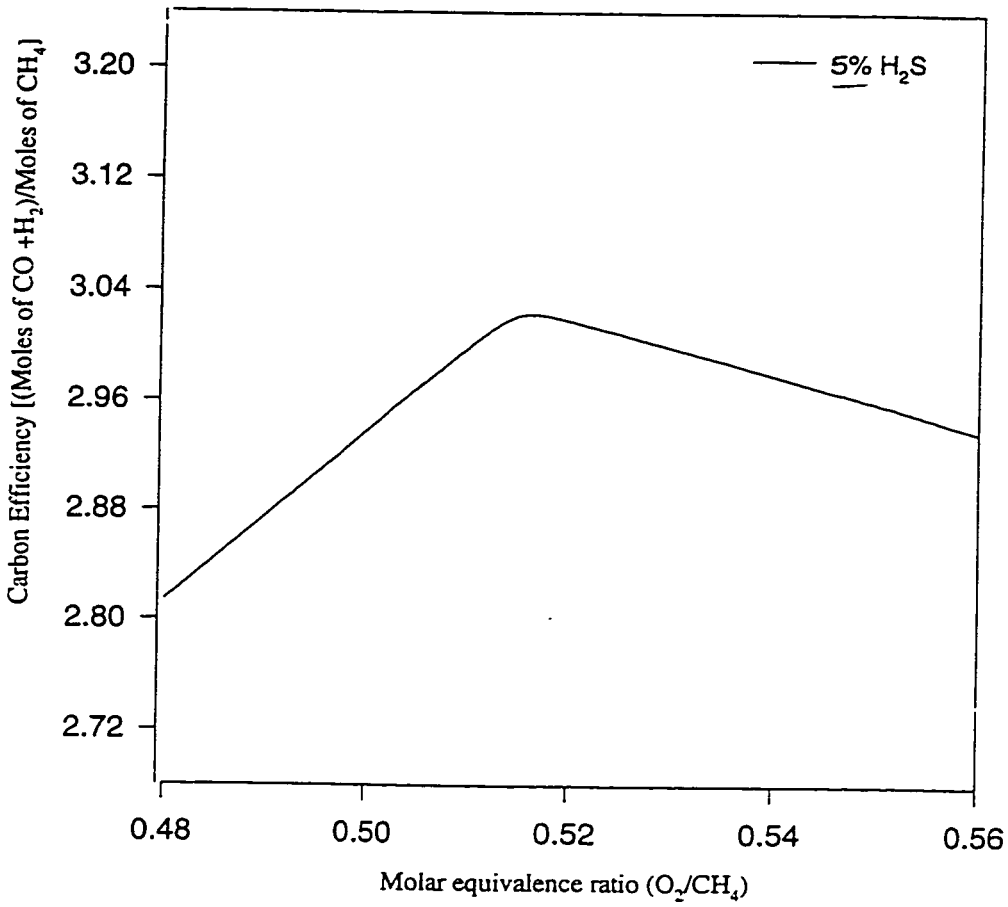


Figure 6.13 Variation of carbon efficiency with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 48-56

The carbon efficiency is a parameter, which signifies the conversion of the hydrocarbons achieved in the process of partial oxidation.

6.5.2 Effect of hydrogen sulfide content in feed

The content of hydrogen sulfide in the sour natural gas has profound effect on the carbon efficiency and the number of moles of carbon monoxide and hydrogen in the product. The number of moles of carbon monoxide and hydrogen decrease with the increase in the hydrogen sulfide content of the sour natural gas. So, the carbon efficiency also decreases with the increase in the hydrogen sulfide content of the feed as shown in Figure 6.14. The partial oxidation of the hydrogen sulfide is highly exothermic. The partial oxidation of the hydrogen sulfide does not produce any carbon monoxide and hydrogen whereas methane and other hydrocarbons produce carbon monoxide upon partial oxidation. So, there is a decrease in the carbon monoxide and hydrogen production with the increase in the hydrogen sulfide content of the feed. Hence, there is a decrease in the carbon efficiency with the increase in the hydrogen sulfide content of the feed.

6.5.3 Effect of heavier hydrocarbon in feed

The number of moles of the carbon monoxide and hydrogen increases with the increase in the content of the heavier hydrocarbon in the feed. But, the carbon efficiency decreases with the increase in the heavier hydrocarbon content of the feed as shown in Figure 6.15. The heavier hydrocarbons, like ethane and propane have higher ratios of carbon to hydrogen compared to methane, so upon oxidation they produce higher number of moles

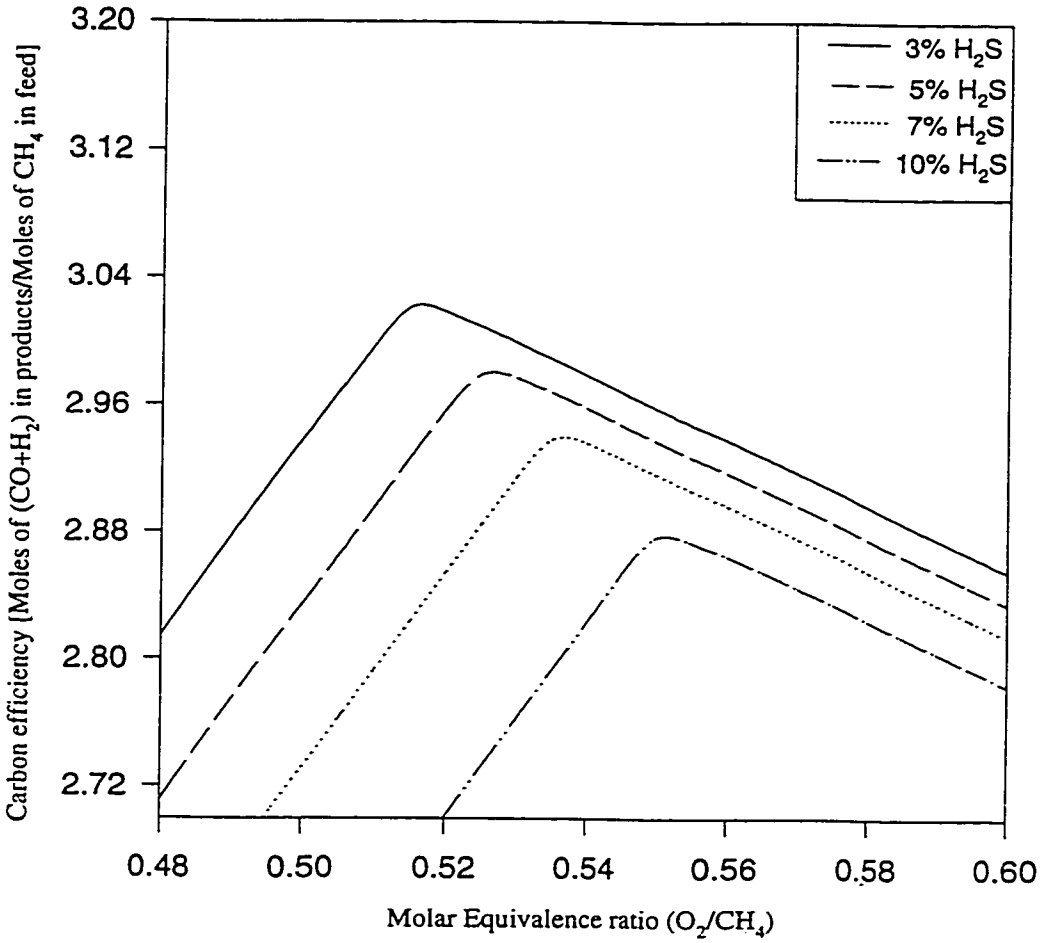


Figure 6.14 Effect of H_2S content on the carbon efficiency

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 90-97, moles H_2S 10-3, moles O_2 48-60

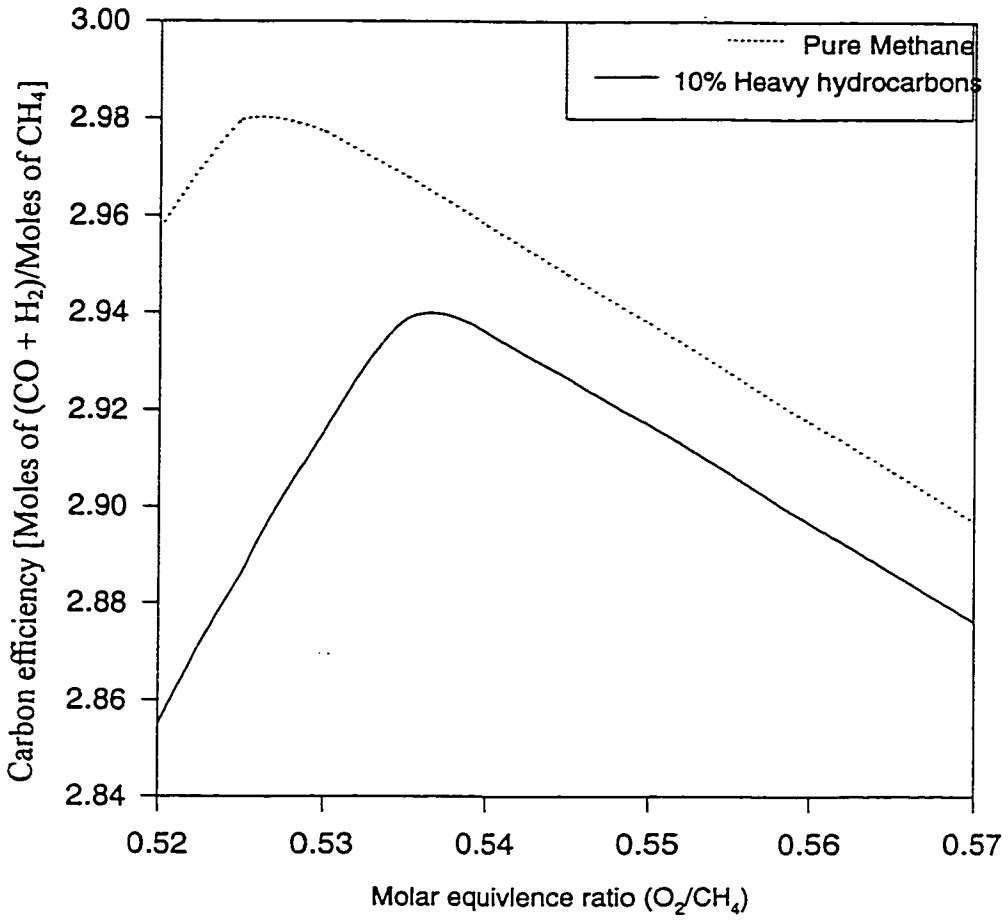


Figure 6.15 Effect of heavier hydrocarbons than methane on the carbon efficiency

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 80-90, moles H_2S 10, moles O_2 52-57, moles C_2H_6 5-0, moles C_3H_8 5-0

of carbon monoxide, but lower number of moles of hydrogen compared to that produced by methane. Hence, the carbon efficiency is lower.

6.5.4 Effect of preheat temperature

The number of moles of carbon monoxide and hydrogen is lower for lower preheat temperature of natural gas as shown in Figure 6.16. Higher preheat temperature results in high hydrocarbon conversion, as the higher temperature favors the endothermic secondary reactions. Hence, the carbon efficiency is higher in case of higher preheat temperature of natural gas. Preheat of oxygen also improves number of moles of carbon monoxide, hydrogen and carbon efficiency.

Carbon efficiency can be increased by increasing the conversion of the hydrocarbon by reducing the heat loss from the combustion chamber by providing insulation from heat.

6.5.5 Effect of pressure

Increase in the pressure lowers the number of moles of carbon monoxide as shown in Figure 6.17. Increase in the pressure adversely affects the secondary reactions 3.3 and 3.4, resulting in the lower number of moles of carbon monoxide in the product. Hence, any increase in the pressure decreases the carbon efficiency. The disadvantages of pressure operation lie in the adverse effect on equilibrium and the severe mechanical problems that will be introduced in this high temperature process.

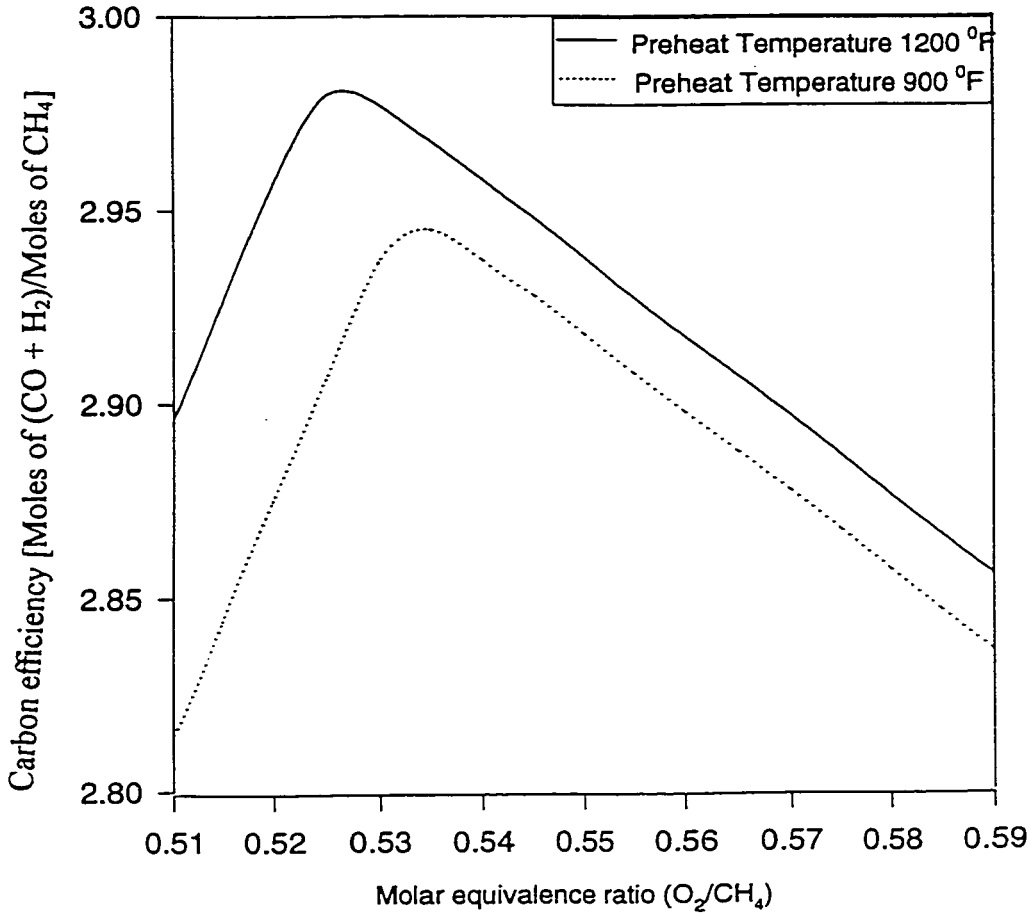


Figure 6.16 Effect of preheat temperature on the carbon efficiency

Operating Conditions
Temperature = 2200 °F
Pressure = 15 psi
Preheat Temperature = 1200 °F and 900 °F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 51-59

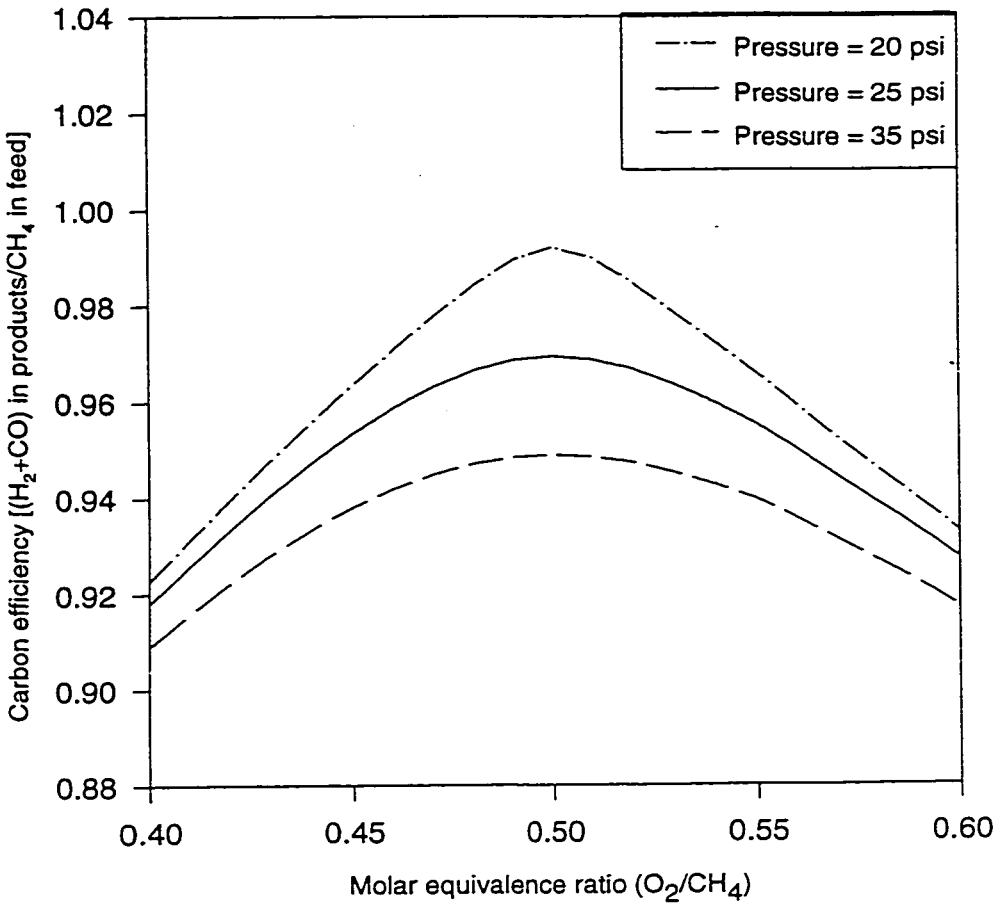


Figure 6.17 Effect of the pressure on the carbon efficiency

Operating Conditions
Temperature = 2200 ^{0}F
Pressure = 20 psi, 25psi, 35psi
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 40-60

6.6 Oxygen Efficiency

The oxygen efficiency depends upon a number of parameters. Oxygen efficiency is the ratio of the sum of the moles of the hydrogen and carbon monoxide in the product to the number of the moles of the oxygen in the feed. It depends on the number of moles of the hydrogen and carbon monoxide. Hydrogen and carbon monoxide is formed in the second stage when carbon dioxide and steam reacts with unreacted methane. Hence, number of moles of hydrogen and carbon monoxide depend upon the amount of carbon dioxide and steam produced and methane left unreacted in the first stage. Oxygen efficiency also depends on the same parameters as the carbon efficiency.

6.6.1 Effect of equivalence ratio

Effect of Equivalence ratio on the oxygen efficiency shows the same pattern as the number of moless of the hydrogen and carbon monoxide. It increases gradually then reaches a maximum then decreases as shown in the Figure 6.18. This maximum occurs at ER = 0.525.

After reaching the maximum at the optimum molar equivalence ratio, the oxygen efficiency decreases sharply. The oxygen supply in feed is increased steadily; however the number of moles of the hydrogen and carbon monoxide in the product decreases. This is due to the fact that more oxygen reacts with methane to produce carbon monoxide and steam less methane is left to react with carbon dioxide and steam to carbon monoxide and

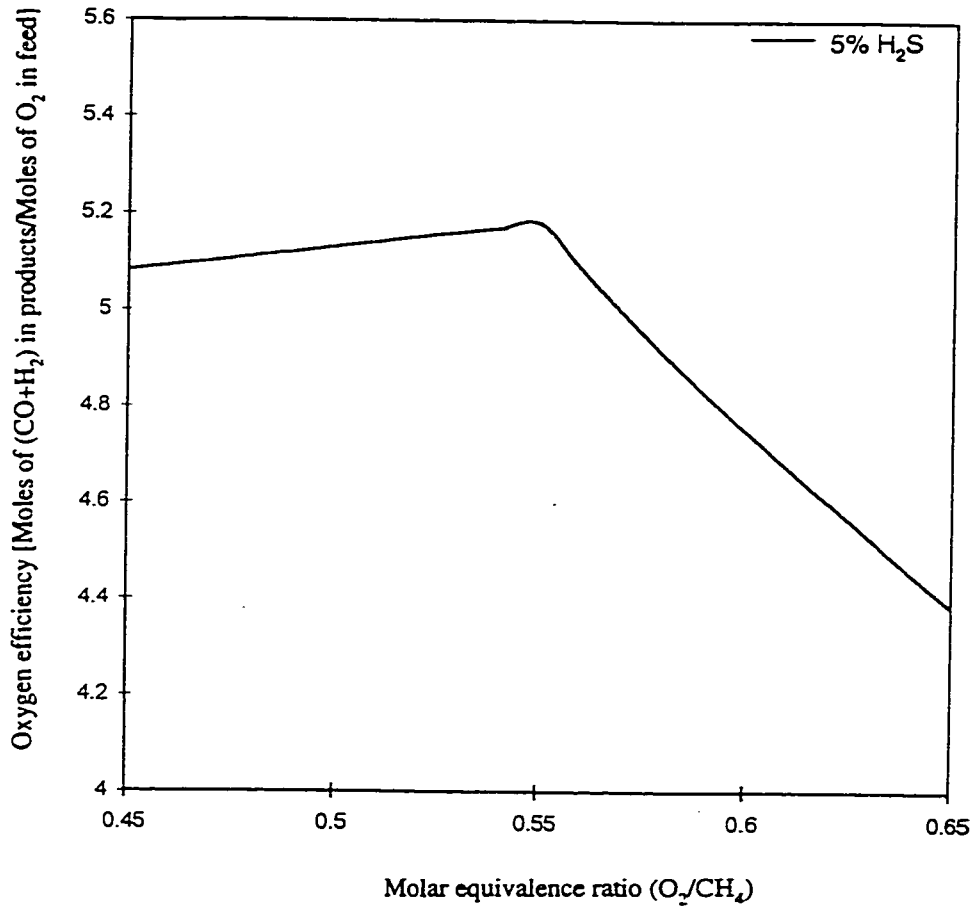


Figure 6.18 Variation of the oxygen efficiency with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 48-56

hydrogen. Hence, the carbon monoxide and hydrogen decreases and amount of carbon dioxide and steam increase in the product. Thus, a steady increase in the supply of oxygen in the feed induces a decline of hydrogen and carbon monoxide in the product, contributing to a sharp decrease in the oxygen efficiency.

6.6.2 Effect of hydrogen sulfide content in feed

The content of hydrogen sulfide in the sour natural gas has direct effect on the oxygen efficiency. The number of moles of hydrogen and carbon monoxide in the product decrease with the increase in the hydrogen sulfide content of the sour natural gas as shown in Figure 6.2 and Figure 6.7 respectively. So, the oxygen efficiency also decreases with the increase in the hydrogen sulfide content of the feed as shown in Figure 6.19. The partial oxidation of the hydrogen sulfide does not produce any carbon monoxide and hydrogen whereas methane and other hydrocarbons produce carbon monoxide upon partial oxidation. So, there is a decrease in the carbon monoxide and hydrogen production with the increase in the hydrogen sulfide content of the feed. Hence, there is a decrease in the oxygen efficiency with the increase in the hydrogen sulfide content of the feed.

6.6.3 Effect of heavier hydrocarbons in the feed

The number of moles of carbon monoxide and hydrogen in the product increases with the increase in the content of the heavier hydrocarbons in the feed. But, the oxygen efficiency decreases with the increase in the heavier hydrocarbon content of the feed as shown in the Figure 6.20. The heavier hydrocarbons contain more atoms of carbon monoxide

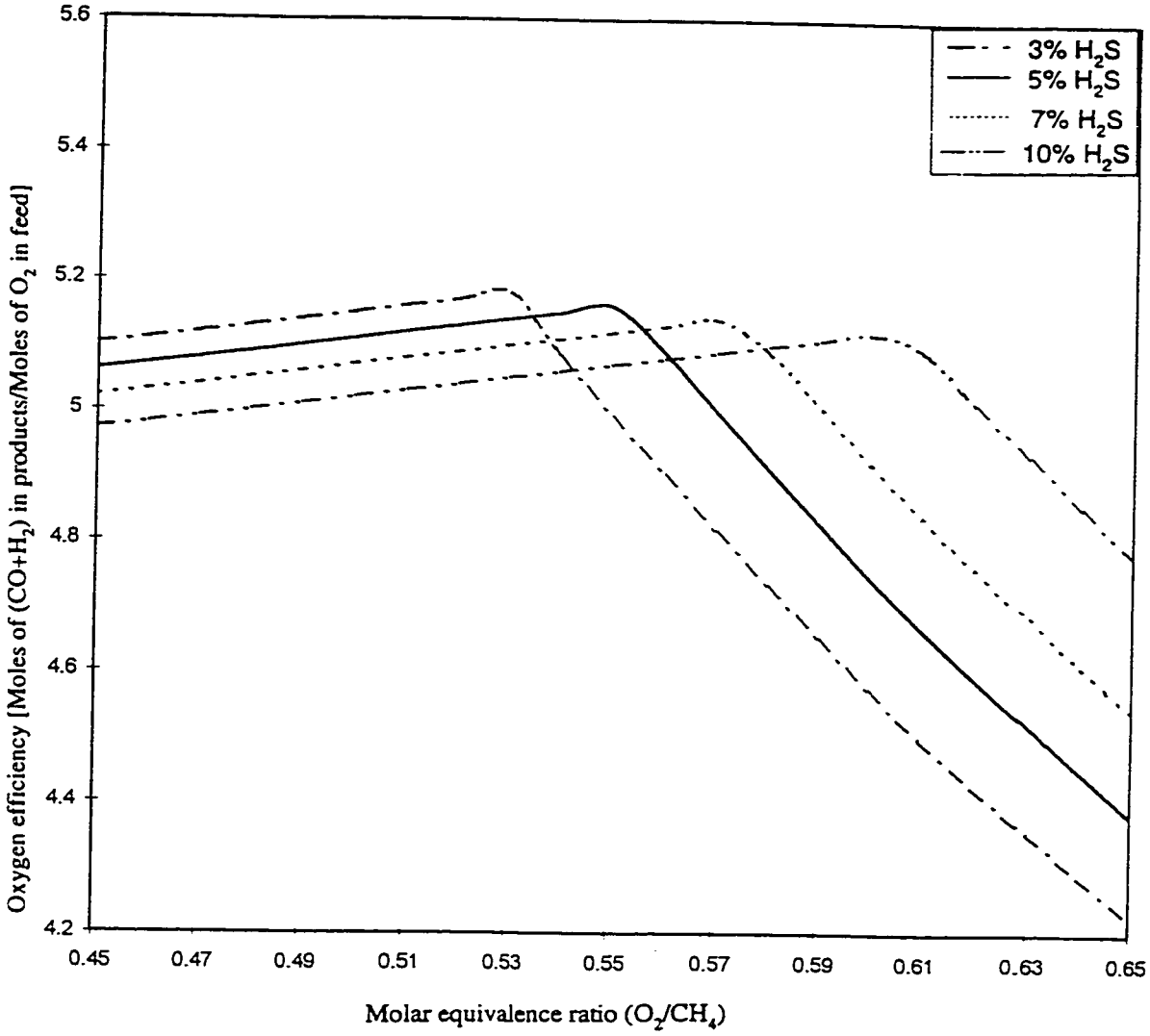


Figure 6.19 Effect of the H_2S content on the oxygen efficiency

<u>Operating Conditions</u>
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 90-97, moles H_2S 10-3, moles O_2 49-59

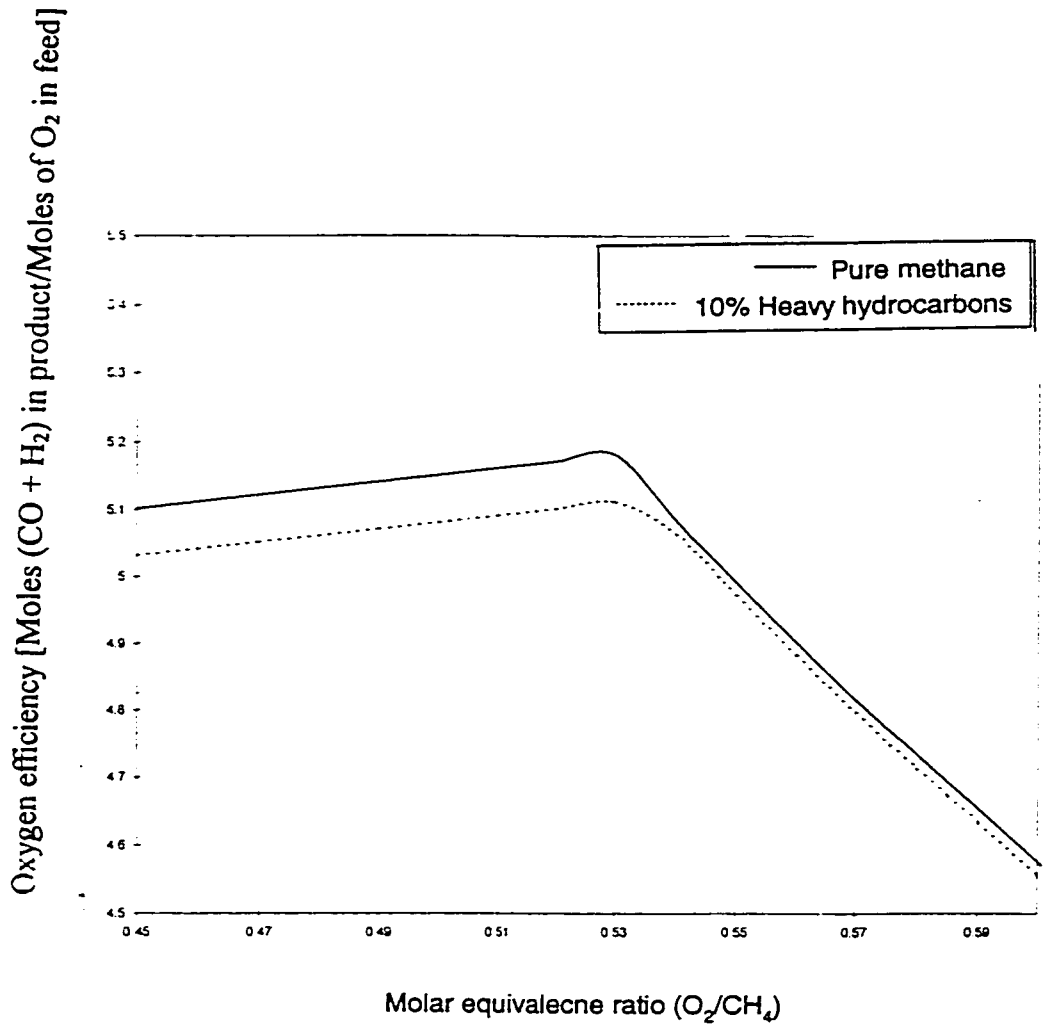


Figure 6.20 Effect of heavy hydrocarbons on the oxygen efficiency

Operating Conditions

Pressure = 15 psi

Temperature = 2200 ^{0}F

Preheat Temperature = 1200 ^{0}F

Feed = moles CH_4 80-90, moles H_2S 10, moles O_2 52-57, moles C_2H_6 5-0, moles C_3H_8 5-0

compared to methane, so upon oxidation gives higher number of moles of carbon monoxide and hydrogen. But, the number of moles of the hydrogen is relatively lower than that obtained with the pure methane. Hence, the oxygen efficiency is lower.

6.6.4 Effect of preheat temperature

The number of moles of carbon monoxide and hydrogen is lower for lower preheat temperature of natural gas. Higher preheat temperature results in high hydrocarbon conversion, as the higher temperature favors the endothermic secondary reactions. Hence, the oxygen efficiency is higher in case of higher preheat temperature of natural gas as shown in the Figure 6.21. Preheat of oxygen also improves the number of moles of carbon monoxide and hydrogen in the product and the oxygen efficiency.

6.6.5 Effect of pressure

Increase in the pressure lowers the number of moles of carbon monoxide in the product. Increase in the pressure adversely affects the secondary reactions 3.3 and 3.4, resulting in a lower number of moles of carbon monoxide. Hence, any increase in the pressure decreases the oxygen efficiency. The disadvantages of pressure operation lie in the adverse effect on equilibrium and the severe mechanical problems that will be introduced in this high temperature process.

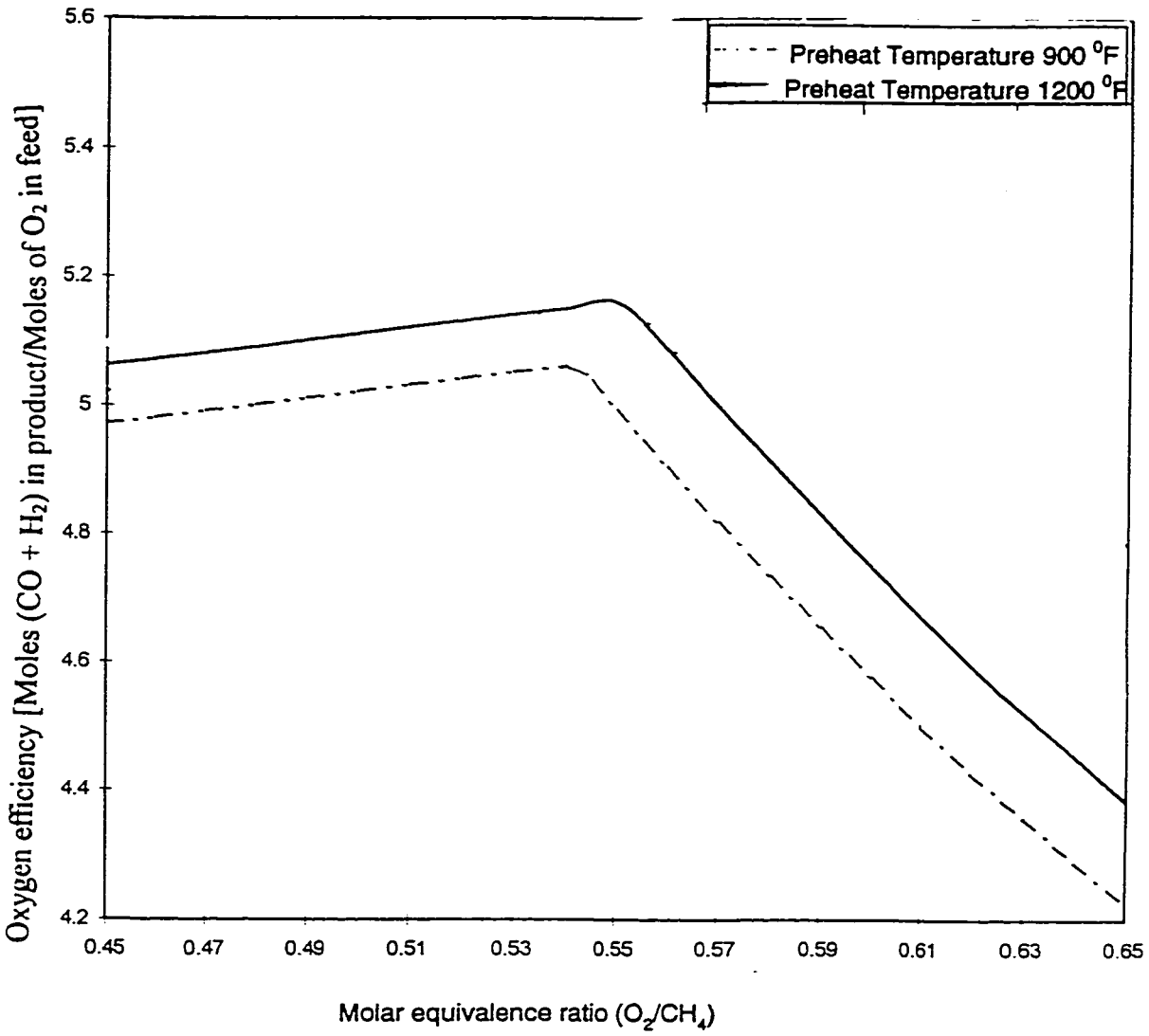


Figure 6.21 Effect of preheat temperature on the oxygen efficiency

Operating Conditions
Temperature = 2200 ^{0}F
Pressure = 15 psi
Preheat Temperature = 1200 ^{0}F and 900 ^{0}F
Feed = moles CH_4 95, moles H_2S 5, moles O_2 51-56

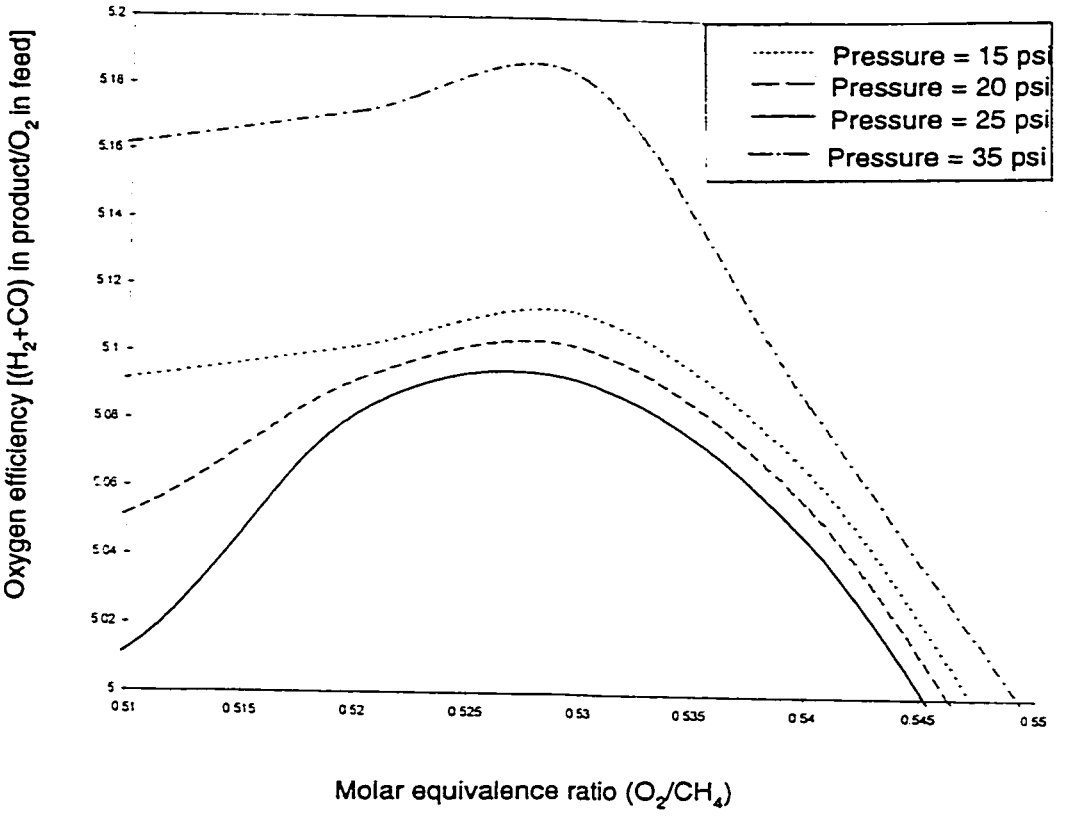


Figure 6.22 Effect of pressure on the oxygen efficiency

Operating Conditions
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Pressure = 15psi, 20 psi, 25psi, 35psi
Feed = moles CH_4 100, moles O_2 40-60

6.7 Simulation Results (Mathematical Modeling)

The effect of the Equivalence ratio on the number of moles of the H_2 and CO in the product is shown in Figure 6.23 and 6.24. The number of moles increased initially with the increasing Equivalence ratio but it reaches a maximum and then decreases. The conversion of oxygen is observed to be complete. The results of FORTRAN simulation are in good agreement with the results of the ASPENPlus simulation as shown in the Figures 6.25 to 6.27.

As a results of the validation of the ASPENPlus simulation results, it is apparent that the use of either of the procedure leads to same results. This leads to an insight into the procedure followed by the ASPENPlus for the simulation, i.e. developing mass, heat/enthalpy balances etc.

After validation this system model developed on the ASPENPlus can be used in simulation of the whole flowsheet.

6.8 Validation

- The model cannot be validated by data reported in the literature related to the non catalytic partial oxidation of the sour natural gas. However, Mungen and Kratzer [1951] have reported data of a pilot plant studies of the non-catalytic partial oxidation of sweet natural gas. So, the model was modified for the sweet natural gas and the

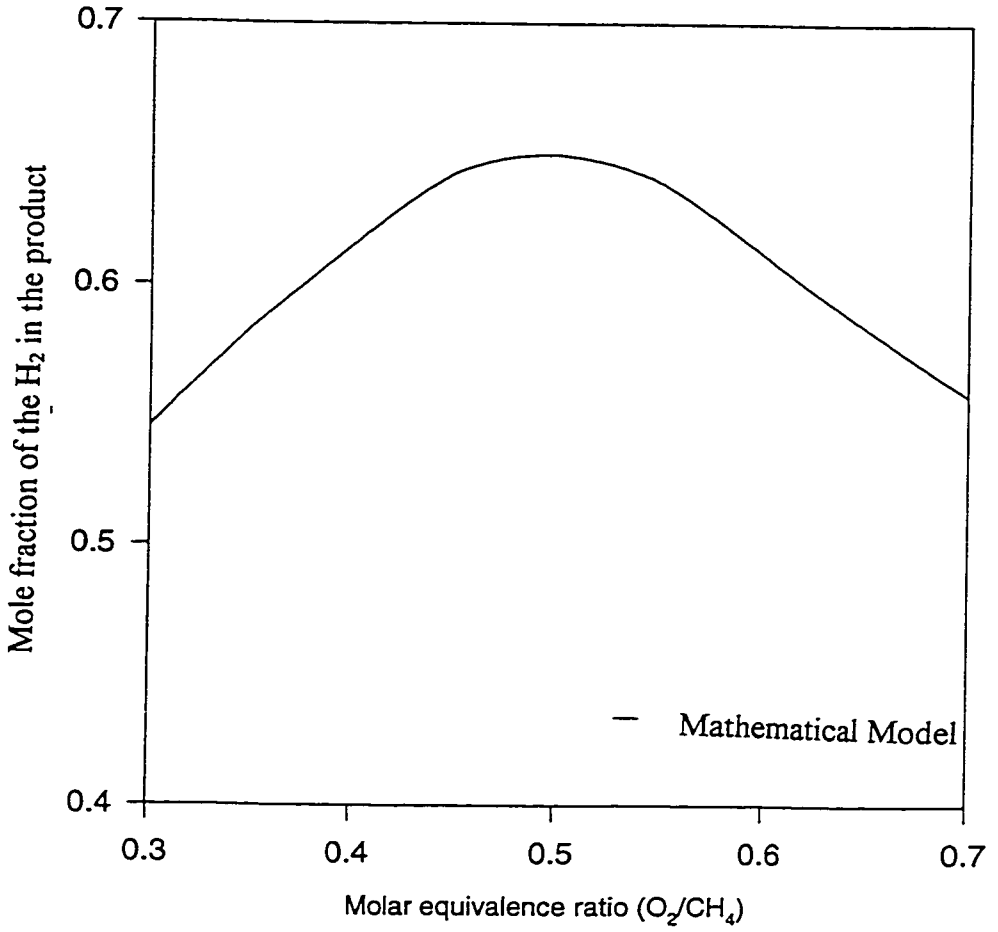


Figure 6.23 Variation of the number of moles of hydrogen with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 30-70

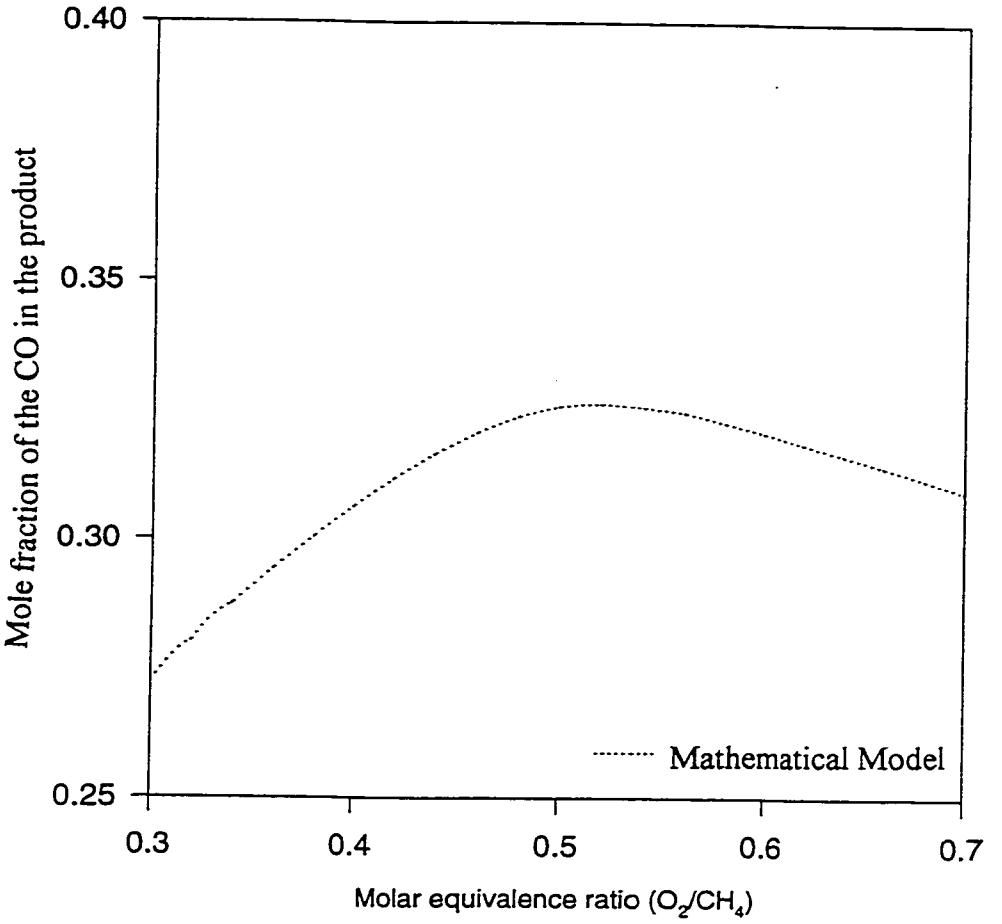


Figure 6.24 Variation of the number of moles of carbon monoxide with the molar equivalence ratio

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 30-70

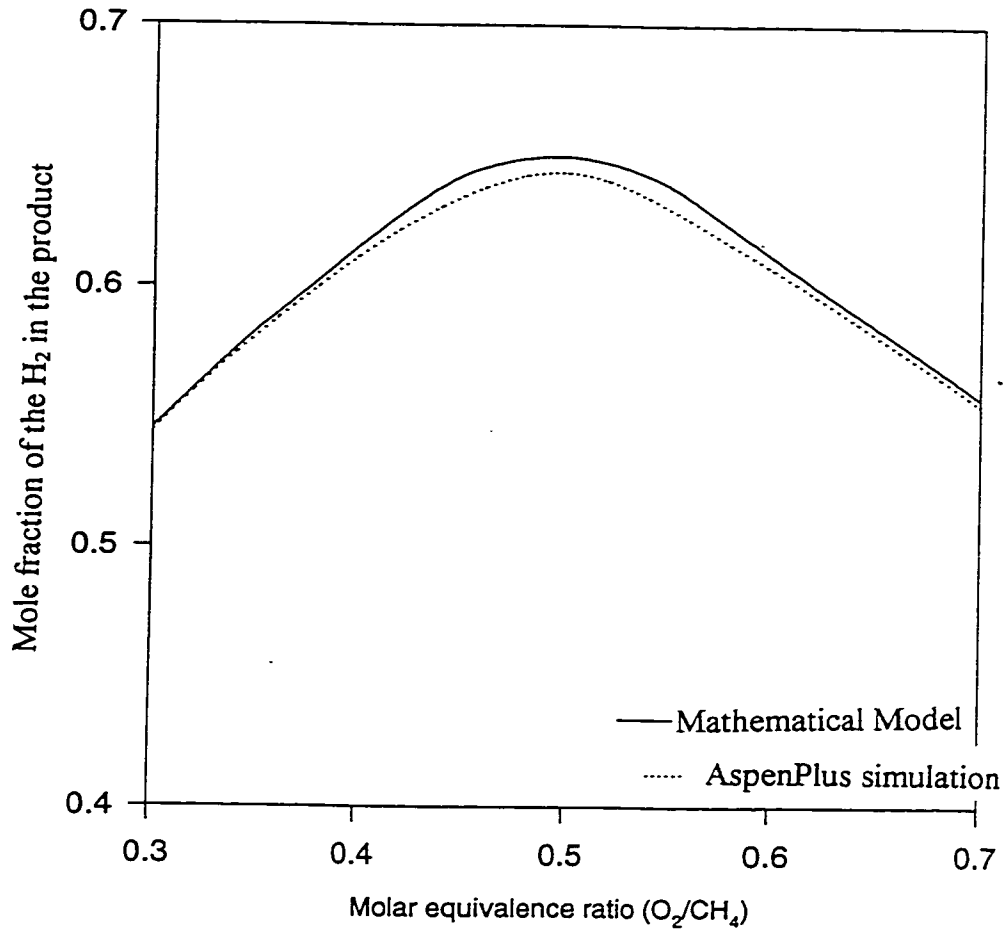


Figure 6.25 Comparison of AspenPlus simulation with results of mathematical model (number of moles of H_2)

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 30-70

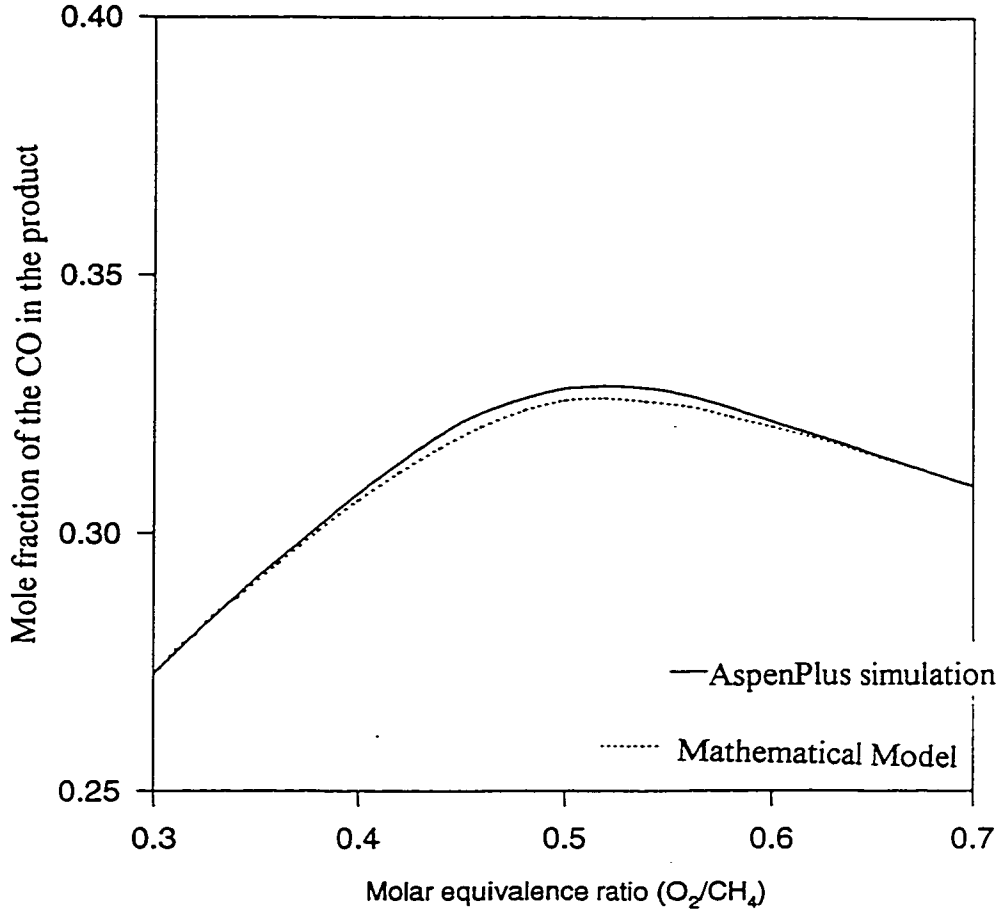


Figure 6.26 Comparison of AspenPlus simulation with results of mathematical model [number of moles of CO in the product]

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 30-70

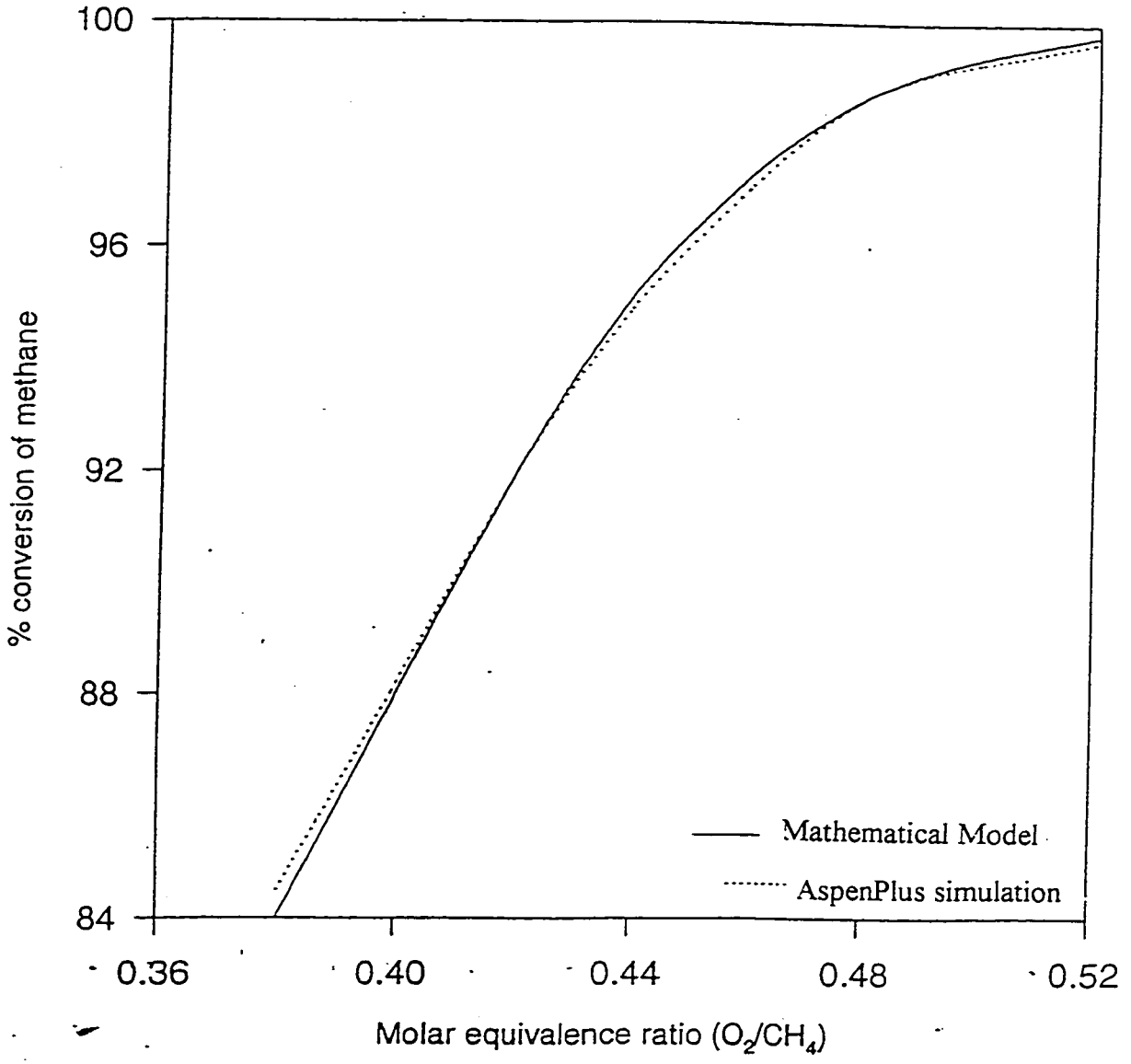


Figure 6.27 Comparison of AspenPlus simulation with results of mathematical model (% conversion of methane)

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 36-42

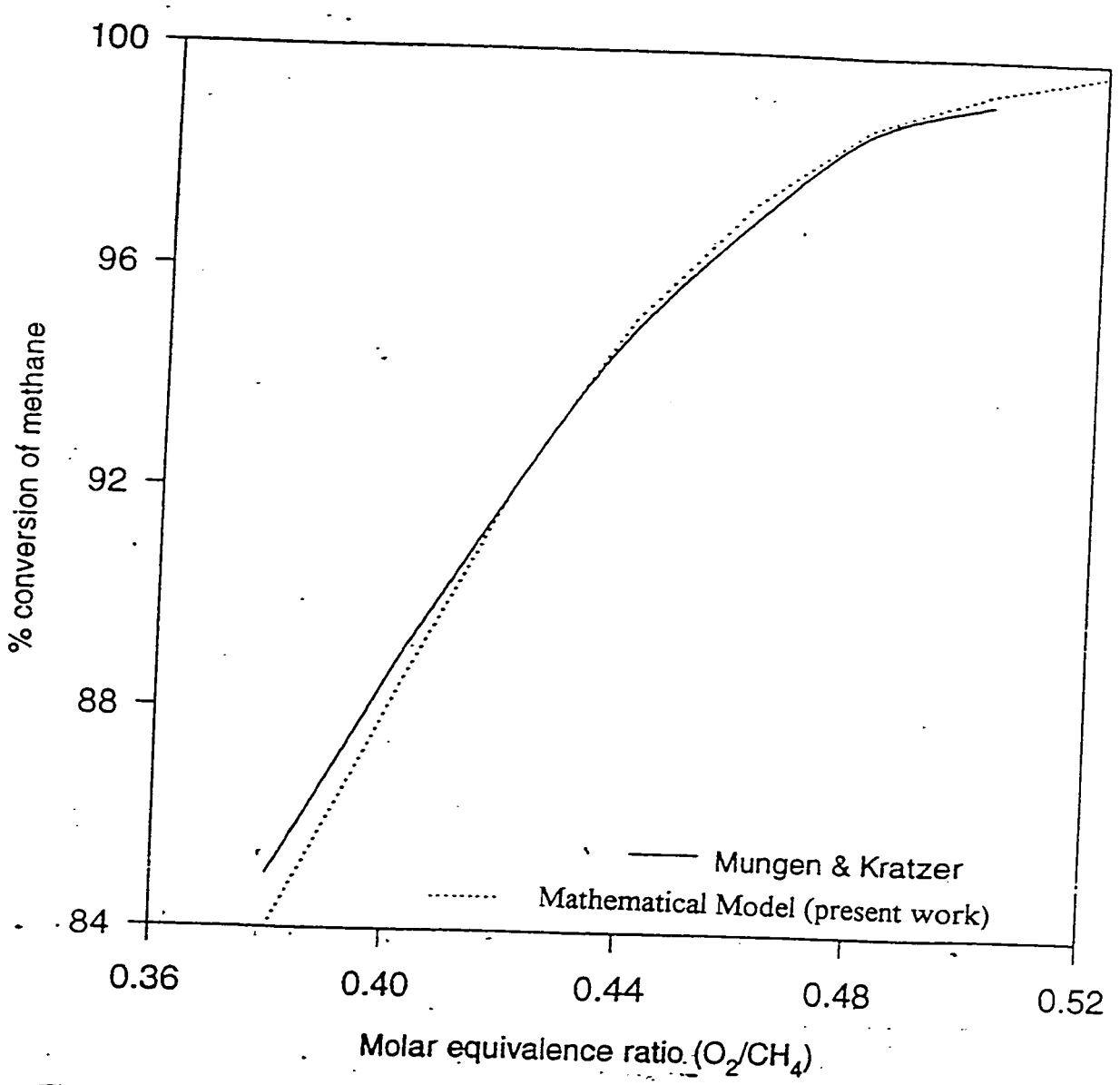


Figure 6.28 Comparison of results of mathamaticl model with published work (% conversion of methane)

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 36-52

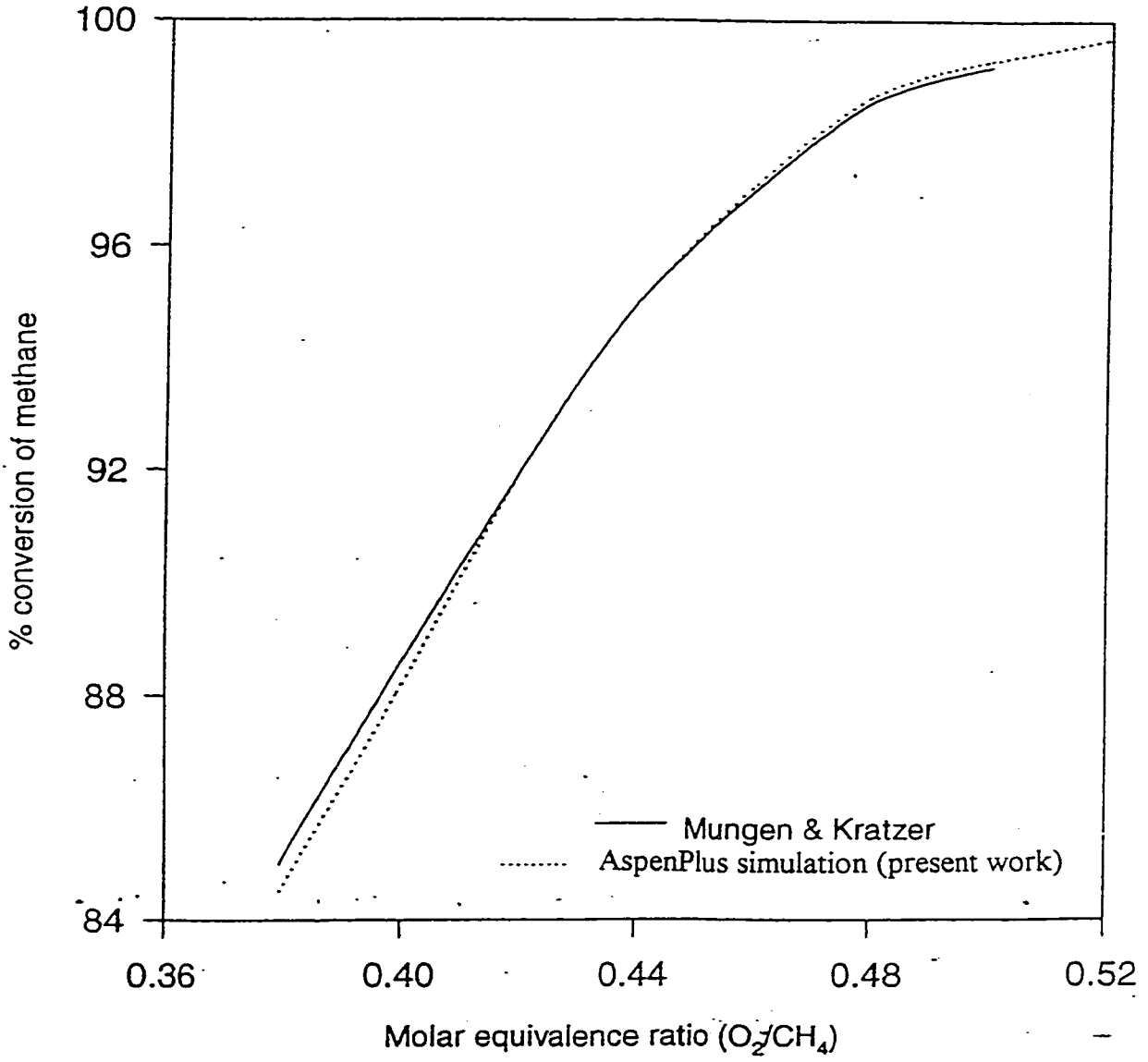


Figure 6.29 Comparison of AspenPlus simulation with published work (% conversion of methane)

Operating Conditions
Pressure = 15 psi
Temperature = 2200 ^{0}F
Preheat Temperature = 1200 ^{0}F
Feed = moles CH_4 100, moles O_2 36-52

simulation was carried out by keeping all the conditions same as that kept by Mungen and Kratzer [1951] as shown in Figure 6.28 and Figure 6.29.

Conditions

- Gas preheat Temperature = 1200 ^{0}F
- Oxygen preheat Temperature = 600 ^{0}F
- Nitrogen in the Feed natural gas = 16 %
- Purity of the Oxygen fed = 93 %Pressure of the combustion chamber = 15 Psig
- Oxidant = Oxygen
- Feed = Sweet Natural Gas

The effect of equivalence ratio on the % methane conversion (AspenPlus simulation) follows the same trend and shows a good agreement with the data of the published work.

6.9 Recommended Operating Parameters

The parameters like molar equivalence ratio, operating temperature of combustion chamber, preheat temperature and operating pressure of the combustion chamber should be maintained at their optimum level. The optimum values of these parameters is presented in the Table 6.3.

6.10 Comparison of the Simulation Result With the Plant Data of a Petrochemical Plant (Ibn Sina)

Upon comparing the proposed process with the steam reforming process of Ibn Sina plant

of Jubail, it is concluded that the feed natural gas of the steam reforming process is lower, because the hydrogen in the synthesis gas comes from the steam dissociation in the process of steam-reforming. However, a substantial amount of the nautral gas is burnt as fuel to supply the necessary heat to the endothermic reforming process. The effluent gas from the fuel burner is vented to atmosphere. The combined amount of the feed and fuel gas for the steam-reforming process is more than the feed gas of the non catalytic partial oxidation. Also, the heat recovered in the proposed process of non catalytic partial oxidation is approximately two and half times the amount of heat recovered in the steam reforming. The calculation for the proposed process is carried out by keeping the basis of calculation the same i.e., Product synthesis gas.

Table 6.3 Recommended optimum operating parameters

#	OPERATING PARAMETR	OPTIMUM VALUES
1	Molar Equivalence Ratio	0.5*
2	Combustion Chamber Temperature	2200 ^{0}F
3	Combustion Chamber Pressure	15 psi
4	Preheat Temperature	1200 ^{0}F

Table 6.4 Comparison of the results of the proposed process with the plant data

	Ibn Sina, Jubail	**Proposed Process**
	Steam Reforming	**Partial Oxidation**
Feed natural gas	50 MMScfd (sweet)	75 MMScfd (sour)
Fuel	30 MMScfd	0 MMScfd
Feed steam	200 MMScfd	0 MMScfd
Product synthesis gas	194 MMScfd	194 MMScfd
Heat input from furnace	1240 MMBtu/hr	0
Radiant section	676.5MMBtu/hr	0
Convection	563.5 MMBtu/hr	0
Waste heat reacovered	645 MMbtu/hr	1615 MMBtu/hr
Synthesis gas composition	H_2 = .453	H_2 = 0.5479
	CO = .081	CO = 0.3643
	CO_2 = .056	CO_2 = 0.0035
	H_2O = .01	H_2O = 0.065
	CH_4 = .001	CH_4 = 0
	N_2 = .399	N_2 = 0
	SO_2 =0	SO_2 =0.0193

PART B. Waste Heat Recovery and Sulfur dioxide Absorption

6.11 Waste Heat Recovery System

The effluent gases from the combustion chamber are to be directed to a network of waste heat recovery system, before directing to the sulfur dioxide absorption system. In order to illustrate the sequence of events in the integrated system, a typical case is chosen :

For a Feed of 75 MMCuft./Day of Sour Natural Gas [H_2S = 5%]

		Input		**Output**
Conditions				
Temperature [F]		1000.0	2200.0	
Pressure [PSI]		15.00	15.00	
Composition	%Vol.	MMCuft/Day	%Vol.	MMCuft/Day
CH_4	95	71.25	0	0.000
H_2S	5	3.75	0	0.000
H_2	0	0.000	54.94	106.875
CO	0	0.000	36.63	71.25
H_2O	0	0.000	6.5	12.64
SO_2	0	0.000	1.93	3.75
O_2	50	41.25	0	0
		131.25		194.515

Heat Recovered [MMBtu/hr] 1615

The heat recovery system consists of the following equipment :

1. Waste heat exchanger
2. Economizer

An important feature of this process is the capability of recovering much of the heat in the combustion chamber product gas by generating high-pressure steam. The hot gas from the

combustion chamber flows directly to a waste-heat exchanger of special design where it passes through helical coils mounted in the exchanger shell. The sum of the sensible heat recovered from the combustion chamber effluent gas (by raising steam) plus the potential heat of combustion represented by the product gas itself is equal to about 95% of the hydrocarbon feedstock heating value. The use of helical tubes and proper gas velocity gives very long service life without the need for periodic cleaning and without impairment of heat transfer. The steam is generated at a pressure at least 150 psi greater than the combustion chamber pressure so that it can be used directly as moderating steam. Waste-heat exchangers for the partial oxidation process could be designed for steam pressures to about 1500 psig.

The gas leaves the waste-heat exchanger at a temperature somewhat greater than the generated steam temperature. Additional heat is recovered from the gas in an economizer by heat exchange with feed water for the waste-heat exchanger. The split of heat recovery duties between the waste-heat exchanger and the economizer is optimized during the design phase of the partial oxidation process. The temperature of the effluent synthesis gas drops to 35 ^{0}C from the 2200 ^{0}F, such that it is fed to the sulfur dioxide absorption system.

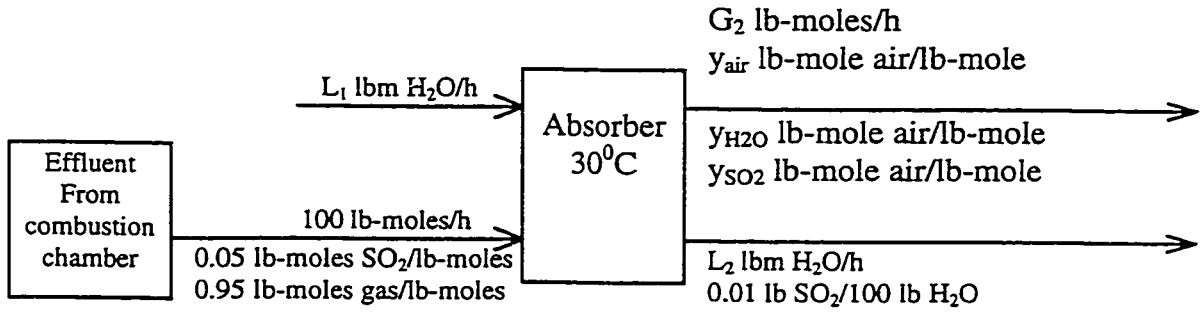
6.12 Absorption of Sulfur dioxide

The effluent gases of the combustion chamber are scrubbed by water. The operation is carried out counter-currently. The water is fed from the top and the effluent gases from

the combustion chamber is fed from the bottom of the absorption tower. An aqueous solution of the sulfur dioxide (Sulfurous acid) will be formed. This solution is a feedstock to the sulfur-cycle or modified Westinghouse process. Sulfur dioxide will be dissolved in water in accordance with Henry's law. The concentration of the sulfur dioxide is reduced from the inlet concentration of 0.05 lb-moles SO_2/lb-moles to effluent sulfur dioxide concentration of 0.002632 $\frac{\text{lb} - \text{moles } SO_2}{\text{lb} - \text{moles}}$. Fresh Water Requirement is 3032603.9 $\frac{\text{lb}_m}{\text{h}}$. The amount of sulfurous acid produced (Aqueous Solution of SO_2 and Water) produced is 3032832.282 $\frac{\text{lb}_m}{\text{h}}$.

Details of the results are given as follows:

Basis : 100 lb-mole/h of effluent gas from the combustion chamber



The equilibrium partial pressures of H_2O and SO_2 at a temperature over a solution of the indicated composition are

$p_{H_2O} = 31.8$ mmHg

$p_{SO_2} = 0.84$ mmHg

so that the composition of the exit gas stream is

$$y_{H_2O} = \frac{31.8\ mmHg}{760\ mmHg} = 0.04184\ \frac{lb-moles\ H_2O}{lb-moles}$$

$$y_{SO_2} = \frac{0.84\ mmHg}{760\ mmHg} = 0.002632\ \frac{lb-moles\ SO_2}{lb-moles}$$

$$y_{gas} = 1 - y_{H_2O} - y_{SO_2} = 0.955526\ \frac{lb-moles\ gas}{lb-moles}$$

Three unknown process variables remain - L_1, G_2 and L_2 - and since a total of three independent balances can be written, the system is determinate.

Gas Balance

$$G_2 * y_{gas} = 0.95 * 100\ \frac{lb-moles\ gas}{h}$$

for $y_{gas} = 0.955526$

$$G_2 = 99.42\ \frac{lb-moles\ gas}{h}$$

To write the two remaining balances, it is necessary to determine the mass fractions of SO_2 and H_2O in the liquid effluent.

$$x_{SO_2} = \frac{0.01\,lb_m\ SO_2}{100.01\,lb_m} = 0.00009999\ \frac{lb_m\ SO_2}{lb_m}$$

$$x_{H_2O} = 0.99991001\ \frac{lb_m\ H_2O}{lb_m}$$

SO_2 Balance

$$G_2 = 99.42\ \frac{lb-moles\ gas}{h}$$

$y_{SO_2} = 0.002632$

$x_{SO_2} = 0.00009999$

$L_2 * x_{SO_2} = [\ 100 * 0.05 - G_2 * y_{H_2O}\ ] * 64$

$$L_2 = 3032832.282\ \frac{lb_m}{h}$$

H_2O Balance

$$G_2 = 99.42\ \frac{lb - moles\ gas}{h}$$

$$y_{H2O} = 0.04184\ \frac{lb - moles\ H_2O}{lb - moles}$$

$$x_{H_2O} = 0.99991001\ \frac{lb_m\ H_2O}{lb_m}$$

$$L_2 = 3032832.282\ \frac{lb_m}{h}$$

$L_1 = G2 * y_{H_2O} * 18 + L_2 * x_{H_2O}$

$$L_1 = 3032603.9\ \frac{lb_m}{h}$$

Fraction SO_2 Absorbed

SO_2 absorbed $= L_2 * x_{SO_2}$

$$= 303.253\ \frac{lb_m\ SO_2\ absorbed}{h}$$

SO_2 fed $= 100 * 0.05 * 64$

$$= 320 \ \frac{lb_m \, SO_2 \, fed}{h}$$

$$\% \text{ Absorbed } SO_2 = \frac{320 - 303.253}{320} * 100 = 94.77 \%$$

Effluent SO_2 concentration

$$y_{SO_2} = 0.002632 \ \frac{lb - moles \, SO_2}{lb - moles}$$

Area of the tower

$$\frac{3 \ x \ 10^6 \ \frac{lb \, H_2O}{hr}}{62.5 \ \frac{lb}{ft^3}} = 48{,}000 \ ft^3/hr$$

Assume velocity of 1 ft/hr = 3600 ft/hr

$$A = \frac{48000}{3600} \approx 13.3 \ ft^3$$

Summary of Results

Effluent gas SO_2 concentration $\quad y_{SO_2} = 0.002632 \ \frac{lb - moles \, SO_2}{lb - moles}$

% Absorbed $SO_2 = 94.77 \%$

Fresh Water Required $\quad L_1 = 3032603.9 \ \frac{lb_m}{h}$

Aqueous Solution of SO_2 and Water produced $L_2 = 3032832.282 \frac{lb_m}{h}$

A weak aqueous solution of SO_2 and Water (Sulfurous Acid) is produced which is concentrated by absorbing SO_2 produced from the oxidation of the elemental sulfur. The concentration of the SO_2 in the water is brought to the requirement of the modified Westinghouse process.

6.13 Open Sulfur-cycle Process

This is an open electrochemical cycle also known as Westinghouse process. Since the supply of the SO_2 is continuous, it is more beneficial to use open sulfur-cycle instead of closed sulfur-cycle. Open sulfur-cycle is similar to closed sulfur-cycle except that decomposition of H_2SO_4 is eliminated. Hydrogen is produced along with sulfuric acid in a low temperature electrochemical step:

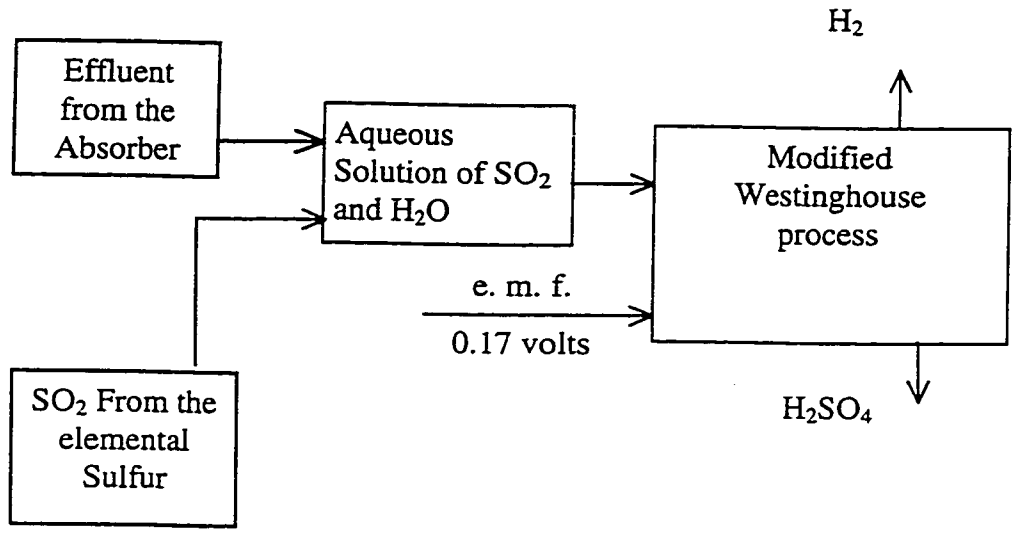
$$2H_2O\,(l) + SO_2\,(aq) \rightarrow H_2SO_4\,(aq) + H_2\,(g) \qquad 298K\,(0.17V)$$

The open sulfur-cycle continuously produces sulfuric acid as a main product. The produced sulfuric acid has to be concentrated using a multi-staged flashing before it is sold as a concentrated acid.

Although electrical power is required in the electrochemical step, much smaller quantities then those necessary for water electrolysis is needed. The theoretical voltage to

decompose water is 1.23V, with many commercial electrolyzers requiring only 2.0V. The power requirements for reaction 1 (0.17 Volts), are theoretically less than 15% of those required in conventional electrolysis. The cell voltage of 600-800 mV obtainable in a practical sulfurous acid electrolyzer would only require some 30-40% of the electrical power of advanced water electrolyzers.

Hydrogen is generated electrolytically in an electrolysis cell which anodically oxidizes sulfurous acid to sulfuric acid while simultaneously generating hydrogen at the cathode.



Aqueous Solution of SO_2 and Water fed $L_2 = 3032832.282 \frac{lb_m}{h}$

Hydrogen produced from the modified Westinghouse process = $61239.88 \frac{lb_m}{h}$

Sulfuric acid produced = $2974508.31 \frac{lb_m}{h}$

CHAPTER 7

CONCLUSIONS AND RECOMMENDATION

1. A two-stage reaction mechanism is proposed and simulated for the partial combustion of sour natural gas: first oxygen reacts with some of the methane and the hydrogen sulfide to produce carbon dioxide, water and sulfur dioxide followed by the reactions of carbon dioxide and water with the rest of the methane to give carbon monoxide and hydrogen.
2. Using this scheme of non catalytic partial oxidation (NCPO), simulation is carried out using two different approaches:
   - ASPENPLUS: stages 1 and 2 of the mechanism are simulated on by RSTOIC and REQUIL respectively.
   - Mathematical modeling based on the mass balance, enthalpy balance and equilibrium relationships.

3. Results obtained using both simulation techniques are in good agreement with the work published by Mungen and Kratzer for the partial oxidation of sweet natural gas.
4. The transformation of hydrogen sulfide into sulfur dioxide, hence sulfuric acid along with the production of synthesis gas via NCPO offers a novel scheme that could compete with conventional steam reforming with the elimination of the expensive gas desulfurization process.
5. The optimum conversion of the sour natural gas is achieved in the vicinity of one-half molar equivalence ratio depending on the content of hydrogen sulfide in the feed of sour natural gas.
6. Other typical values o operating parameters are: preheat temperature of 1200^0F, operating combustion chamber temperature of 2200^0F, and a pressure of 15 psi
7. The presence of heavier hydrocarbons and hydrogen sulfide in the feed sour natural gas lowers the yield of synthesis gas and carbon efficiency.
8. The proposed process is recommended for ammonia and urea production from sour natural gas. Partial oxidation takes place-using air, which provides nitrogen, used in ammonia fixation.
9. For methanol production, where synthesis gas consists only of carbon monoxide and hydrogen, partial oxidation process of sour natural gas has to be implemented using pure oxygen. Economics of such a process has to be considered carefully.
10. The proposal offers a new approach to produce sulfuric acid via non-catalytic process, known as the open sulfuric cycle along with additional hydrogen, thus increasing the yield of synthesis gas.

11. The potential of implementing this scheme in the future particularly in Saudi Arabia could be strengthened by carrying out experimental work on the NCPO of sour natural gas, followed by an economic feasibility study.
12. The proposal could bring in substantial advantages and savings for the Master Gas System currently employing steam reforming process with acidic gas treatment facilities.

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APPENDICES

APPENDIX A
Computer Code for Simulation (AspenPlus)

```
                                    TM
AAAAA  SSSSS  PPPPP  EEEEE  NN   N  PPPPP  L      U     U  SSSSS
A   A  S      P   P  E      NN N N  P   P  L      U     U  S
AAAAA  SSSSS  PPPPP  EEEEE  N NN N  PPPPP  L      U     U  SSSSS
A   A      S  P      E      N  NN N  P      L      U     U      S
A   A  SSSSS  P      EEEEE  N   N  P      LLLLL  UUUUU  SSSSS
```

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617/577-0100

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U.S.A. 617/577-0337
EUROPE (32) 2/726-9303

VERSION: PC-DOS
RELEASE: 9.2-1
INSTALLATION: FAHDU-PC

DECEMBER 31, 1996
TUESDAY
3:06:27 P.M.

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RUN CONTROL SECTION

RUN CONTROL INFORMATION

THIS COPY OF ASPEN PLUS LICENSED TO KING FAHD UNIV

TYPE OF RUN: NEW

INPUT FILE NAME: _3506blg.inm

OUTPUT PROBLEM DATA FILE NAME: _0516blg VERSION NO. 1
LOCATED IN:
PDF SIZE USED FOR INPUT TRANSLATION:
NUMBER OF FILE RECORDS (PSIZE) = 0
NUMBER OF IN-CORE RECORDS = 256
PSIZE NEEDED FOR SIMULATION = 1

CALLING PROGRAM NAME: apmain

SIMULATION REQUESTED FOR ENTIRE FLOWSHEET

ASPEN PLUS VER: PC-DOS REL.: 9.2-1 INST: FAHDU-PC 12/31/96 PAGE 2

FLOWSHEET SECTION

FLOWSHEET CONNECTIVITY BY STREAMS

STREAM	SOURCE	DEST	STREAM	SOURCE	DEST
7	—	B3	2	B1	B2
3	B1	B2	4	B2	—
5	B2	—	6	B2	—
8	B3	B1			

FLOWSHEET CONNECTIVITY BY BLOCKS

BLOCK	INLETS	OUTLETS
B1	8	2 3
B2	2 3	4 5 6
B3	7	8

COMPUTATIONAL SEQUENCE

SEQUENCE USED WAS:
S-1 B3 *B1 B2
(RETURN S-1)

OVERALL FLOWSHEET BALANCE

*** MASS AND ENERGY BALANCE ***

	IN	OUT	GENERATION	RELATIVE DIFF.
CONVENTIONAL COMPONENTS (LBMOL/HR)				
CH4	90.0000	0.119249E-03	-89.9999	0.543547E-16
O2	100.000	0.000000E+00	-100.000	0.000000E+00
H2S	10.0000	0.000000E+00	-10.0000	0.000000E+00
H2	0.000000E+00	117.800	117.800	0.000000E+00
CO	0.000000E+00	72.2013	72.2013	0.000000E+00
CO2	0.000000E+00	17.8000	17.8000	0.000000E+00
H2O	0.000000E+00	72.2002	72.2002	0.000000E+00
SO2	0.000000E+00	10.0000	10.0000	0.000000E+00
TOTAL BALANCE				
MOLE(LBMOL/HR)	200.000	290.001	90.0014	0.000000E+00
MASS(LB/HR)	4984.55	4984.59		-0.849145E-05
ENTHALPY(BTU/HR)	0.194961E+07	-289411.		1.14845

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SENSITIVITY BLOCK SECTION

SENSITIVITY BLOCK: S-1

SAMPLED VARIABLES:
XCH4 : CH4 MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XO2 : O2 MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XH2S : H2S MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XH2 : H2 MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XCO : CO MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XCO2 : CO2 MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XH2O : H2O MOLEFLOW IN STREAM 4 SUBSTREAM MIXED
XSO2 : SO2 MOLEFLOW IN STREAM 4 SUBSTREAM MIXED

VARIED VARIABLES:
VARY 1: O2 MOLEFLOW IN STREAM 7 SUBSTREAM MIXED
LOWER LIMIT = 5.0000 LBMOL/HR
UPPER LIMIT = 200.0000 LBMOL/HR
INCREMENT = 5.0000

TABULATED VARIABLES:
COLUMN 2: XCH4
COLUMN 3: XO2
COLUMN 4: XH2S
COLUMN 5: XH2
COLUMN 6: XCO
COLUMN 7: XCO2
COLUMN 8: XH2O
COLUMN 9: XSO2

VARY 1	XCH4	XO2	XH2S	XH2	XCO
7					
MIXED					
O2 MOLEF					
LOW					
LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR
5.0000	86.6666	0.0	6.6666	10.0000	3.3352
10.0000	83.3333	0.0	3.3333	20.0000	6.6874
15.0000	80.0000	0.0	0.0	30.0000	10.0044
20.0000	70.0000	0.0	0.0	49.9999	20.0000
25.0000	60.0000	0.0	0.0	69.9999	30.0116

SENSITIVITY BLOCK SECTION

SENSITIVITY BLOCK: S-1 (CONTINUED)

VARY 1	XCH4	XO2	XH2S	XH2	XCO
7					
MIXED					
O2 MOLEF					
LOW					
LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR
30.0000	50.0001	0.0	0.0	89.9996	40.0031
35.0000	40.0002	0.0	0.0	109.9992	50.0008
40.0000	30.0006	0.0	0.0	129.9982	59.9997
45.0000	20.0016	0.0	0.0	149.9960	69.9986
50.0000	10.0045	0.0	0.0	169.9888	79.9955
55.0000	0.2303	0.0	0.0	189.3457	89.7328
60.0000	4.6162-03	0.0	0.0	181.6245	85.3741
65.0000	1.9775-03	0.0	0.0	173.3457	86.6758
70.0000	1.1217-03	0.0	0.0	165.1427	84.9073
75.0000	7.1083-04	0.0	0.0	157.0247	83.0608
80.0000	4.7662-04	0.0	0.0	148.9854	81.0702
85.0000	3.3018-04	0.0	0.0	141.0420	79.0153
90.0000	2.3299-04	0.0	0.0	133.1814	76.8186
95.0000	1.6628-04	0.0	0.0	125.4367	74.5637
100.0000	1.1925-04	0.0	0.0	117.7997	72.2012
105.0000	8.5558-05	0.0	0.0	110.2760	69.7257
110.0000	6.1186-05	0.0	0.0	102.8711	67.1318
115.0000	4.3473-05	0.0	0.0	95.5907	64.4140
120.0000	3.0590-05	0.0	0.0	88.4407	61.5670
125.0000	2.1250-05	0.0	0.0	81.4272	58.5858
130.0000	1.4523-05	0.0	0.0	74.5564	55.4654
135.0000	9.7278-06	0.0	0.0	67.8353	52.2018
140.0000	6.3574-06	0.0	0.0	61.2715	48.7918
145.0000	4.0162-06	0.0	0.0	54.8176	45.1823
150.0000	2.4470-06	0.0	0.0	48.5574	41.4427
155.0000	1.4210-06	0.0	0.0	42.4626	37.5379
160.0000	7.7588-07	0.0	0.0	36.5375	33.4643
165.0000	3.9062-07	0.0	0.0	30.7863	29.2194
170.0000	1.7600-07	0.0	0.0	25.2145	24.8032
175.0000	6.7607-08	0.0	0.0	19.8324	20.2224
180.0000	1.9886-08	0.0	0.0	14.5842	15.4161
185.0000	3.6771-09	0.0	0.0	9.5452	10.4598
190.0000	2.1483-10	0.0	0.0	4.6817	5.3185
195.0000	0.0	1.8000	0.0	1.6788	1.9516
200.0000	0.0	6.8000	0.0	1.6798	1.9527

SENSITIVITY BLOCK SECTION

SENSITIVITY BLOCK: S-1 (CONTINUED)

VARY 1	XCH4	XO2	XH2S	XH2	XCO

O2 MOLEF					
LOW					
LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR
w 100.0000	1.1925-04	0.0	0.0	117.7997	72.2012

VARY 1	XCO2	XH2O	XSO2
7			
MIXED			
O2 MOLEF			
LOW			
LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR
w 5.0000	2.6180-09	1.9518-08	3.3333
w 10.0000	3.6789-08	2.7358-07	6.6666
w 15.0000	1.6443-07	1.2260-06	10.0000
w 20.0000	1.5669-06	9.7393-06	10.0000
w 25.0000	6.2808-06	3.6423-05	10.0000
w 30.0000	1.7721-05	9.9122-05	10.0000
w 35.0000	4.2319-05	2.3146-04	10.0000
w 40.0000	9.4601-05	5.0957-04	10.0000
w 45.0000	2.1762-04	1.1593-03	10.0000
w 50.0000	6.2571-04	3.3055-03	10.0000
w 55.0000	3.6885-02	0.1934	10.0000
w 60.0000	1.6376	8.3671	10.0000
w 65.0000	3.3494	16.6531	10.0000
w 70.0000	5.1419	24.8628	10.0000
w 75.0000	7.0190	32.9884	10.0000
w 80.0000	8.9791	41.0233	10.0000
w 85.0000	11.0346	48.9680	10.0000
w 90.0000	13.1823	56.8181	10.0000
w 95.0000	15.4372	64.5630	10.0000
w 100.0000	17.8000	72.2002	10.0000

SENSITIVITY BLOCK SECTION

SENSITIVITY BLOCK: S-1 (CONTINUED)

VARY 1	XCO2	XH2O	XSO2
7			
MIXED			
O2 MOLEF			
LOW			
LBMOL/HR	LBMOL/HR	LBMOL/HR	LBMOL/HR
w 105.0000	20.2760	79.7242	10.0000
w 110.0000	22.8707	87.1295	10.0000
w 115.0000	25.5896	94.4106	10.0000
w 120.0000	28.4384	101.5618	10.0000
w 125.0000	31.4226	108.5777	10.0000
w 130.0000	34.5478	115.4526	10.0000
w 135.0000	37.8193	122.1812	10.0000
w 140.0000	41.2423	128.7582	10.0000
w 145.0000	44.8176	135.1823	10.0000
w 150.0000	48.5573	141.4426	10.0000
w 155.0000	52.4623	147.5376	10.0000
w 160.0000	56.5365	153.4634	10.0000
w 165.0000	60.7833	159.2166	10.0000
w 170.0000	65.2055	164.7944	10.0000
w 175.0000	69.8052	170.1947	10.0000
w 180.0000	74.5840	175.4159	10.0000
w 185.0000	79.5428	180.4572	10.0000
w 190.0000	84.6816	185.3183	10.0000
195.0000	88.0647	188.3352	10.0000
200.0000	88.0647	188.3352	10.0000

ASPEN PLUS VER: PC-DOS REL: 9.2-1 INST: FAHDU-PC 12/31/96 PAGE 7

PHYSICAL PROPERTIES SECTION

COMPONENTS

ID	TYPE	FORMULA	NAME OR ALIAS	REPORT NAME
CH4	C	CH4	CH4	CH4
O2	C	O2	O2	O2
H2S	C	H2S	H2S	H2S
H2	C	H2	H2	H2
CO	C	CO	CO	CO
CO2	C	CO2	CO2	CO2
H2O	C	H2O	H2O	H2O
SO2	C	O2S	O2S	SO2

ASPEN PLUS VER: PC-DOS REL: 9.2-1 INST: FAHDU-PC 12/31/96 PAGE 8

U-O-S BLOCK SECTION

BLOCK: B1 MODEL: RSTOIC

INLET STREAM: 1
OUTLET STREAM: 2
OUTLET HEAT STREAM: 3
PROPERTY OPTION SET: BWR-LS BWR-LEE-STARLING EQUATION OF STATE

*** MASS AND ENERGY BALANCE ***

	IN	OUT	GENERATION	RELATIVE DIFF.
TOTAL BALANCE				
MOLE(LBMOL/HR)	195.000	195.000	0.137679E-13	0.706045E-16
MASS(LB/HR)	4984.55	4984.55	0.000000E+00	
ENTHALPY(BTU/HR)	-289411.	-289411.		-0.221237E-14

*** INPUT DATA ***

SIMULTANEOUS REACTIONS
STOICHIOMETRY MATRIX:

REACTION # 1:
SUBSTREAM MIXED :
CH4 -1.00 O2 -2.00 CO2 1.00 H2O 2.00

REACTION CONVERSION SPECS: NUMBER= 1
REACTION # 1:
SUBSTREAM:MIXED KEY COMP:CH4 CONV FRAC: 0.9900

TWO PHASE TP FLASH

SPECIFIED TEMPERATURE F	2,200.00
SPECIFIED PRESSURE PSI	15.0000
MAXIMUM NO. ITERATIONS	30
CONVERGENCE TOLERANCE	0.000100000

ASPEN PLUS VER: PC-DOS REL: 9.2-1 INST: FAHDU-PC 12/31/96 PAGE 9

U-O-S BLOCK SECTION

BLOCK: B1 MODEL: RSTOIC (CONTINUED)

*** RESULTS ***

OUTLET TEMPERATURE	F	2200.0
OUTLET PRESSURE	PSI	15.000
HEAT DUTY	BTU/HR	-0.14707E+08
VAPOR FRACTION		1.0000

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
CH4	0.24359	0.18526	0.24359	3205.8
CO2	0.21795	0.17094	0.21795	3112.0
H2O	0.48718	0.60764	0.48718	1957.2
SO2	0.51282E-01	0.36160E-01	0.51282E-01	3461.8

BLOCK: B2 MODEL: REQUIL

```
 OUTLET VAPOR STREAM:  4
 OUTLET LIQUID STREAM:  5
 OUTLET HEAT STREAM:  6
 PROPERTY OPTION SET:  BWR-LS   BWR-LEE-STARLING EQUATION OF STATE

          *** MASS AND ENERGY BALANCE ***
              IN       OUT     GENERATION  RELATIVE DIFF.
 TOTAL BALANCE
 MOLE(LBMOL/HR)      195.000    290.001     95.0014   -0.196011E-15
 MASS(LB/HR )       4984.55    4984.59                -0.349145E-05
 ENTHALPY(BTU/HR )  -289411.   -289411.               -0.543036E-14
********************************************************************************
ASPEN PLUS  VER: PC-DOS  REL: 9.2-1  INST: FAHDU-PC 12/31/96 PAGE 10

              U-O-S BLOCK SECTION

BLOCK: B2     MODEL: REQUIL (CONTINUED)

            *** INPUT DATA ***
 TWO  PHASE TP FLASH
 SPECIFIED TEMPERATURE F                  2,200.00
 SPECIFIED PRESSURE  PSI                  15.0000
 MAXIMUM NO. ITERATIONS                   30
 CONVERGENCE TOLERANCE                    0.000100000
 LIQUID ENTRAINMENT                       0.00000E+00
 SOLID SPLIT FRACTIONS:
 SUBSTREAM NO. =  1  MIXED SUBSTREAM, NO SOLID SPLITS.

            *** RESULTS ***
 OUTPUT TEMPERATURE  F                    2200.0
 OUTPUT PRESSURE     PSI                  15.000
 HEAT DUTY           BTU/HR               0.49496E+07
 VAPOR FRACTION                           1.0000


BLOCK: B3     MODEL: RSTOIC
------------------------------
 INLET STREAM:         7
 OUTLET STREAM:        8
 PROPERTY OPTION SET:  BWR-LS   BWR-LEE-STARLING EQUATION OF STATE

          *** MASS AND ENERGY BALANCE ***
              IN       OUT     GENERATION  RELATIVE DIFF.
 TOTAL BALANCE
 MOLE(LBMOL/HR)      200.000    195.000    -5.00000   0.142109E-15
 MASS(LB/HR )       4984.55    4984.55                0.182463E-15
 ENTHALPY(BTU/HR )  0.194961E+07 -289411.              1.14845
********************************************************************************
ASPEN PLUS  VER: PC-DOS  REL: 9.2-1  INST: FAHDU-PC 12/31/96 PAGE 11

              U-O-S BLOCK SECTION

BLOCK: B3     MODEL: RSTOIC (CONTINUED)

            *** INPUT DATA ***

 SIMULTANEOUS REACTIONS
 STOICHIOMETRY MATRIX:

 REACTION #  1:
 SUBSTREAM MIXED  :
 O2     -1.50  H2S     -1.00  H2O      1.00  SO2      1.00


 REACTION CONVERSION SPECS: NUMBER=  1
  REACTION #  1:
  SUBSTREAM:MIXED   KEY COMP:H2S    CONV FRAC:  1.000


 TWO  PHASE TP FLASH
 SPECIFIED TEMPERATURE F                  2,200.00
 SPECIFIED PRESSURE  PSI                  15.0000
 MAXIMUM NO. ITERATIONS                   30
 CONVERGENCE TOLERANCE                    0.000100000

            *** RESULTS ***
 OUTLET TEMPERATURE  F                    2200.0
 OUTLET PRESSURE     PSI                  15.000
 HEAT DUTY           BTU/HR               -0.22390E+07
 VAPOR FRACTION                           1.0000
```

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
CH4	0.46154	0.43107	0.46154	2439.8
O2	0.43590	0.44763	0.43590	2219.2
H2O	0.51282E-01	0.73264E-01	0.51282E-01	1594.8
SO2	0.51282E-01	0.48036E-01	0.51282E-01	2432.8

ASPEN PLUS VER: PC-DOS REL: 9.2-1 INST: FAHDU-PC 12/31/96 PAGE 12

STREAM SECTION

2 4 5 7 8

STREAM ID	2	4	5	7	8
FROM :	B1	B2	B2	—	B3
TO :	B2	—	—	B3	B1
SUBSTREAM: MIXED					
PHASE:	VAPOR	VAPOR	MISSING	VAPOR	VAPOR
COMPONENTS: LBMOL/HR					
CH4	47.5000	1.1925-04	0.0	90.0000	90.0000
O2	0.0	0.0	0.0	100.0000	85.0000
H2S	0.0	0.0	0.0	10.0000	0.0
H2	0.0	117.7997	0.0	0.0	0.0
CO	0.0	72.2012	0.0	0.0	0.0
CO2	42.5000	17.8000	0.0	0.0	0.0
H2O	95.0000	72.2002	0.0	0.0	10.0000
SO2	10.0000	10.0000	0.0	0.0	10.0000
TOTAL FLOW:					
LBMOL/HR	195.0000	290.0014	0.0	200.0000	195.0000
LB/HR	4984.5472	4984.5895	0.0	4984.5472	4984.5472
CUFT/HR	3.7108+05	5.5193+05	0.0	3.8065+05	3.7113+05
STATE VARIABLES:					
TEMP F	2200.0000	2200.0000	MISSING	2200.0000	2200.0000
PRES PSI	15.0000	15.0000	15.0000	15.0000	15.0000
VFRAC	1.0000	1.0000	MISSING	1.0000	1.0000
LFRAC	0.0	0.0	MISSING	0.0	0.0
SFRAC	0.0	0.0	MISSING	0.0	0.0
ENTHALPY:					
BTU/LBMOL	-7.6904+04	-3.4644+04	MISSING	9748.0641	-1484.1603
BTU/LB	-3008.5526	-2015.5517	MISSING	391.1313	-58.0617
BTU/HR	-1.4996+07	-1.0047+07	MISSING	1.9496+06	-2.8941+05
ENTROPY:					
BTU/LBMOL-R	10.2745	18.4715	MISSING	10.5685	10.1466
BTU/LB-R	0.4019	1.0746	MISSING	0.4240	0.3969
DENSITY:					
LBMOL/CUFT	5.2549-04	5.2543-04	MISSING	5.2542-04	5.2543-04
LB/CUFT	1.3432-02	9.0312-03	MISSING	1.3095-02	1.3431-02
AVG MW	25.5617	17.1881	MISSING	24.9227	25.5617

ASPEN PLUS VER: PC-DOS REL: 9.2-1 INST: FAHDU-PC 12/31/96 PAGE 13

STREAM SECTION

3 6

STREAM ID	3	6
FROM :	B1	B2
TO :	B2	—
CLASS:	HEAT	HEAT
STREAM ATTRIBUTES:		
HEAT		
Q BTU/HR	1.4707+07	9.7573+06

APPENDIX B
Computer Code for Simulation (Newton-Raphson)

nwraphs.f Sun Oct 27 18:26:53 1996

```
      program main
      dimension xold(21),xinc(21),a(21,21)

c      read and print data
      open(6,FILE = 'nwraphs.out',STATUS = 'old')
  1   read (*,*) itmax,iprint,n,eps1,eps2,(xold(i),i=1,n)
c      write (6,200) itmax,iprint,n,eps1,eps2,n,(xold(i),i=1,n)
c
c      xold(1) = moles of CH4 in the products
c      xold(2) = moles of CO2 in the products
c      xold(3) = moles of H2O in the products
c      xold(4) = moles of CO  in the products
c      xold(5) = moles of H2  in the products
c      xold(6) = moles of O2 in products per mole of CH4 in feed
c      xold(7) = Total moles of products per mole of CH4 in feed
c      xold(8) = Presure of the reactor
c
c
c     INITIAL GUESSES
c  1   itmax   = 100
c      iprint  = 1
c      n       = 8
c      eps1    = 1.0e-10
c      eps2    = 1.0e-5
c      xold(1) = .1
c      xold(2) = .5
c      xold(3) = .5
c      xold(4) = .5
c      xold(5) = .5
c      xold(6) = .5
c      xold(7) = 1.
c      xold(8) = 20
c      newton-raphson iteration
      do  9 iter=1,itmax

c      call on calcn to set up the A matrix
c     n = 9
      call calcn(xold,a,21)

c      call simul to compute jacobian and corrections in xinc
      deter=simul(n,a,xinc,eps1,1,21)
      if ( deter.ne.0. ) go to 3
          write (6,201)
          go to 1

c      check for convergene and update xold values
  3   itcon = 1
      do 5  i=1,n
      if ( abs(xinc(i)).gt.eps2 ) itcon = 0
  5   xold(i) = xold(i) + xinc(i)
      if ( iprint.eq.1 ) write (6,202) iter,deter,n,(xold(i),i=1,n)
      if ( itcon.eq.0 ) go to 9
          write (6,203) iter,n,(xold(i),i=1,n)
          go to 1
  9   continue

c
      write (6,204)
      go to 1
c
c     formats for input and output statements
c 100  format (10x,i3,17x,i1,19x,i3/ 10x,e7.1,13x,e7.1/ (20x,5f10.3))

 200  format (10x,i3,17x,i1,19x,i3/ 10x,e7.1,13x,e7.1/ (20x,5f10.3))
```

```
nwraphs.f        Sun Oct 27 16:26:53 1996
c 200  format (10h1itmax = , i8/ 10h iprint = , i8/ 10h n = ,
c     +    i8/ 10h eps1 = , 1pe14.1/ 10h eps2 = , 1pe14.1/
c     +    26h0   xold(1)....xold(, i2, 1h)/ 1h / (1h , 1p4e16.6))
 201  format (36h0matrix is ill conditioned or singular )
c202  format (10h0iter = , i8/ 10h deter = , e18.5/
c     +   26h     xold(1)...xold(, i2, 1h) / (1h, 1p4e16.6))
 202  format (1x,'iter = ',i8,2x,'deter =',e18.5/,'n =',i2/'xold(1) to
     +xold(7)'/,4e16.6/ 3e16.6)
c203  format (24h0successful convergence / 10h0iter = , i3/
c     +    26h0    xold(1)...xold(, i2, 1h) / 1h /(1h, 1p4e16.6))
 203  format (1x,'iter = ',i8,2x,'n =',i2/'xold(1) to
     +xold(7)'/,4e16.6/ 3e16.6/ 'successful convergence')

c203  format (1x,'successful convergence','iter = ',i8,2x,'deter =',
c     +e18.5,/,'n =',i2,'xold(1) to
c     +xold(7)',4e16.6)
 204  format (15h no convergence )
c
      end
c
c
c
      subroutine calcn( dxold,a,nrc)
c
c
      dimension xold(20),dxold(nrc),a(nrc,nrc)
c
      data p/ 20. /
c
c     shift elements of dxold to xold and clear a array
      do 1 i=1,7
      xold(i) = dxold(i)
      do 1 j=1,8
  1   a(i,j)=0.
c
c     constants
c      k1      =  35.439
c      k2      =  38.092
c      k3      = -2.653
c      Hch4Tr  =  8427
c      Hco2Tr  = -78213
c      Hh2oTr  = -139009
c      HcoTr   = -28837
c      Hh2Tr   =  18927
c      Ho2Tp   =  10690
c      Hch4Tp  = -13492
c     compute non zero elements of a
      a(1,1) = 0.5
      a(1,2) = 1.
      a(1,3) = .5
      a(1,4) = 0
      a(1,5) = 0
      a(1,6) = -1./xold(7)
      a(1,7) = xold(6)/(xold(7)*xold(7))
c      a(1,8) = 0
      a(1,8) = -xold(1)*.5-xold(2)-xold(3)*.5+(xold(6)/xold(7))
c      a(1,10) =
      a(2,1) = 0
      a(2,2) = 0
      a(2,3) = 1.
      a(2,4) = 1.
      a(2,5) = 2.
      a(2,6) = 0
      a(2,7) = 2./(xold(7)*xold(7))
```

```
nwraphs.f        Sun Oct 27 18:26:53 1996

c       a(2,8) = 0
        a(2,8) = -xold(3)-xold(4)-xold(5)*2.+(2./xold(7))
c       a(2,10)=
        a(3,1) = 1.
        a(3,2) = 1.
        a(3,3) = 0
        a(3,4) = 0
        a(3,5) = 1.
        a(3,6) = 0
        a(3,7) = 1./(xold(7)*xold(7))
c       a(3,8) = 0
        a(3,8) = -xold(1)-xold(2)-xold(5)+(1./xold(7))
c       a(3,10)=
        a(4,1) = -28837.
        a(4,2) = -139009.
        a(4,3) = -78213.
        a(4,4) = 18927.
        a(4,5) = 8427.
        a(4,6) = -10690./xold(7)
        a(4,7) = (-13492.+10690.*xold(6))/(xold(7)*xold(7))
c       a(4,8) = 0
        a(4,8) = 28837.*xold(1)+139009.*xold(2)+78213.*xold(3)
     + -18927.*xold(4)-8427.*xold(5)-13492./xold(7)+
     + 10690.*xold(6)/xold(7)
c       a(4,10)=
        a(5,1) = 1.
        a(5,2) = 1.
        a(5,3) = 1.
        a(5,4) = 1.
        a(5,5) = 1.
        a(5,6) = 0
        a(5,7) = 0
c       a(5,8) = 0
        a(5,8) = 1.-xold(1)-xold(2)-xold(3)-xold(4)-xold(5)
c       a(5,10)=
        a(6,1) = p*p*xold(4)**3
        a(6,2) = 0
        a(6,3) = -1.7837e5*xold(5)
        a(6,4) = 3.*p*p*(xold(4)**2)*xold(1)
        a(6,5) = -1.7837e5*xold(3)
        a(6,6) = 0
        a(6,7) = 0
c       a(6,8) = 2.*k1*xold(4)*xold(8)*(xold(5)**3)
        a(6,8) = 1.7837e5*xold(5)*xold(3)-(xold(4)**3)*(p**2)
     + *xold(1)
c       a(6,10)=
c       a(7,1) = -k2*xold(1)
c       a(7,2) = -k2*xold(2)
c       a(7,3) = 0
c       a(7,4) = 2.*xold(4)*(xold(5)**2)*(xold(8)**2)
c       a(7,5) = 2.*(xold(4)**2)*xold(5)*(xold(8)**2)
c       a(7,6) = 0
c       a(7,7) = 0
c       a(7,8) = 2.*(xold(4)**2)*(xold(5)**2)*xold(8)
c       a(7,9) = -(xold(4)**2)*(xold(5)**2)*(xold(8)**2)+k2*xold(1)
c     + *xold(2)
c       a(7,10)=
        a(7,1) = xold(3)
        a(7,2) = -2.6058*xold(4)
        a(7,3) = xold(1)
        a(7,4) = -2.6058*xold(2)
        a(7,5) = 0
        a(7,6) = 0
        a(7,7) = 0
```

```
nwraphs.f        Sun Oct 27 18:26:53 1996
c       a(7,8) = 0
        a(7,8) = 2.6058*xold(4)*xold(2)-xold(3)*xold(1)
c       a(8,10)=
c       a(9,1) =
c       a(9,2) =
c       a(9,3) =
c       a(9,4) =
c       a(9,5) =
c       a(9,6) =
c       a(9,7) =
c       a(9,8) =
c       a(9,9) =
c       a(9,10)=
c
        return
        end
c
c
        function simul(n,a,x,eps,indic,nrc)
c
c
c
        implicit real(a-h,o-z)
        real a,x,eps,simul
        dimension irow(50),jcol(50),jord(50),y(50),a(nrc,nrc),x(n)
c
        max = n
        if ( indic.ge.0) max = n+1
c
c       is n larger than 50
        if (n.le.50) go to 5
        write ( 6,200)
        simul = 0.
        return
c
c       begin elimination procedure
    5   deter = 1.
        do 18 k = 1,n
        km1=k - 1
c
c       search for pivot element
        pivot = 0.
        do 11 i =1,n
        do 11 j =1,n
c
c       scan irow and jcol arrays for invalid pivot subsripts
        if (k.eq.1) go to 9
        do 10 iscan =1,km1
        do 8 jscan =1,km1
      . if ( i.eq.irow(iscan)) go to 11
        if ( j.eq.jcol(jscan)) go to 11
    8    continue
    10   continue
    9   if (abs(a(i,j)).le.abs(pivot)) go to 11
        pivot = a(i,j)
        irow(k) = i
        jcol(k) = j
   11   continue
c
c       insure that selected pivot is larger than eps
        if (abs(pivot).gt.eps ) go to 13
        simul = 0.
        return
c
```

```
nwraphs.f        Sun Oct 27 18:26:53 1996

c     update the determinant value
  13  irowk = irow(k)
      jcolk = jcol(k)
      deter = deter*pivot
c
c     normalize pivot row element
      do 14 j = 1, max
  14  a(irowk,j) = a(irowk,j)/pivot
c
c     carry out elimination and develop inverse
      a(irowk,jcolk) = 1./pivot
      do 18 i = 1,n
      aijck = a(i,jcolk)
      if (i.eq.irowk) go to 18
      a(i,jcolk) = -aijck/pivot
          do 17 j =1,max
          if(j.ne.jcolk)   a(i,j) = a(i,j) - aijck*a(irowk,j)
  17      continue
  18  continue
c
c     order solution values (if any ) and create jord array
      do 20 i =1,n
      irowi = irow(i)
      jcoli = jcol(i)
      jord(irowi) = jcoli
      if (indic.ge.0) x(jcoli) =a(irowi,max)
  20  continue
c
c     adjust sign of determinant
      intch = 0
      nm1=n-1
      do 22 i = 1,nm1
      ip1 = i+1
      do 23 j = ip1,n
      if (jord(j).ge.jord(i)) go to 22
      jtemp = jord(j)
      jord(j) = jord(i)
      jord(i) = jtemp
      intch = intch + 1
  23  continue
  22  continue
      if ( intch/2*2.ne.intch) deter = - deter
c
c     if indic is positive return with results
      if  (indic.le.0) go to 26
      simul = deter
      return
c
c     if indic is negative or zero , unscramble the inverse
c     first by rows
  26  do 28 j = 1,n
      do 27 i = 1,n
      irowi = irow(i)
      jcoli = jcol(i)
  27  continue
      y(jcoli) = a(irowi,j)
      do 25 k = 1,n
      a(k,j) = y(k)
  25  continue
  28  continue
c
c     then by columns
      do 30 i=1,n
      do 29 j=1,n
```

```
nwraphe.f          Sun Oct 27 16:26:53 1996

      irowj = irow(j)
      jcolj = jcol(j)
      y(irowj) = a(i,jcolj)
   29 continue
      do 30 j = 1,n
   30 a(i,j) = y(j)
c
c
c      return for indic negative or zero
      simul = deter
      return
c
c     format for output
  200 format( 10h0n too big)
c
      stop
      end
```

APPENDIX C
Computer Code for Simulation (NEQNF-IMSL)

```
C*************************************************************************
C This is a program to calculate the equilibrium yields of the          *
C Non-catalytic Partial oxidation of sour natural gas by using          *
C the IMSl subroutine NEQNF                                             *
C*************************************************************************
C X(1) = Number of moles of the methane in the feed                     *
C X(2) = Number of moles of the carbon dioxide in the feed              *
C X(3) = Number of moles of the water vapor in the feed                 *
C X(4) = Number of moles of the carbon monoxide in the feed             *
C X(5) = Number of moles of the hydrogen in the feed                    *
C X(6) = Number of moles of the sulfur dioxide in the feed              *
C X(7) = Number of moles of the hydrogen sulfide in the feed per mole of C1 *
C X(8) = Total Number of moles in the feed per mole of C1               *
C ER  = Equivalence Ratio                                               *
C*************************************************************************

C       Declare Variable

        INTEGER     ITMAX, N
        REAL        ERRREL
        PARAMETER   (n=8)

C
        INTEGER             K,NOUT
        REAL        FNORM, X(N), XGUESS(N)

        EXTERNAL            FCN, NEQNF, UMACH

C       Set Values of initial guess

C

        OPEN(5,FILE='ERVARY.OUT',STATUS='UNKNOWN')
        DATA XGUESS/.32, 0.0, 0.0, .618,0.,2.977/

C

        ERRREL = 0.00001
        ITMAX = 100000

C

        CALL UMACH(2,NOUT)

C       FIND THE SOLUTION

        CALL NEQNF(FCN,ERRREL,N,ITMAX,XGUESS,X,FNORM)

C       OUTPUT

C       WRITE (NOUT,99999) (X(K),K=1,N), FNORM
C99999 FORMAT (',THE SOLUTION TO THE SYSTEM IS'/,X = (',7F8.5,
C     &  ')',WITH FNORM =',F15.10,//)
        WRITE (5,10) (X(K),K=1,N), FNORM
```

```
   10   FORMAT ('THE SOLUTION OF THE SYSTEM IS'/,'X=(',6F8.5,
     &')'/,'WITH NORM = 'F15.10,//)

C

      END

C     USER DEFINED SUBROUTINE FCN

      SUBROUTINE  FCN(X,F,N)
      INTEGER           N
      REAL        X(N),f(N)
      DATA        P/20./

C

C     REAL        EXP,SIN
C     INTRINSIC   EXP,SIN
C

            F(1)=2.*X(2)+X(3)+X(4)+2.*X(6)-ER/X(8)
            F(2)=4.*X(1)+2.*X(3)+2.*X(5)-4./X(8)-2.*X(7)/X(8)
            F(3)=X(1)+X(2)+X(4)-1./X(8)
            F(4)=X(6)*X(8)-1.0
            F(5)=X(1)+X(2)+X(3)+X(4)+X(5)+X(6)-1.
            F(6)=-28837.*X(1)-139009.*x(2)-78213.*x(3)+18927.
     &   X(4)+8427.*X(5)-23452.*X(6)-14893.*X(7)/X(8)+13492.
     &   /X(8)-10690*ER/X(8)
            F(7)=P*P*X(1)*X(4)**3. - 1.7837E55*X(3)*X(5)
            F(8)=X(1)*X(3)-2.6058*X(2)*X(4)
      RETURN
      END
```

```
C*************************************************************************
C This is a program to calculate the equilibrium yields of the          *
C Non-catalytic Partial oxidation of sour natural gas by using          *
C the IMSl subroutine NEQNF                                             *
C*************************************************************************
C X(1) = Number of moles of the methane in the feed                     *
C X(2) = Number of moles of the carbon dioxide in the feed              *
C X(3) = Number of moles of the water vapor in the feed                 *
C X(4) = Number of moles of the carbon monoxide in the feed             *
C X(6) = EQUIVALENCE RATIO                                              *
C X(7) = Total Number of moles in the product                           *
C*************************************************************************

C       Declare Variable

        INTEGER     ITMAX, N
        REAL        ERRREL
        PARAMETER   (n=8)

C
        INTEGER             K,NOUT
        REAL        FNORM, X(N), XGUESS(N)

        EXTERNAL            FCN, NEQNF, UMACH

C       Set Values of initial guess

C

        OPEN(5,FILE='ERVARY.OUT',STATUS='UNKNOWN')
        DATA XGUESS/.32, 0.0, 0.0, .618,0.,2.977/

C

        ERRREL = 0.00001
        ITMAX = 100000

C

        CALL UMACH(2,NOUT)

C       FIND THE SOLUTION

        CALL NEQNF(FCN,ERRREL,N,ITMAX,XGUESS,X,FNORM)

C       OUTPUT

C       WRITE (NOUT,99999) (X(K),K=1,N), FNORM
C99999 FORMAT (',THE SOLUTION TO THE SYSTEM IS'/,X = (',7F8.5,
C     &  ')',WITH FNORM =',F15.10,//)
        WRITE (5,10) (X(K),K=1,N), FNORM
   10   FORMAT ('THE SOLUTION OF THE SYSTEM IS'/,'X=(',6F8.5,
     &')'/,'WITH NORM = 'F15.10,//)
```

```
      END

C     USER DEFINED SUBROUTINE FCN

      SUBROUTINE  FCN(X,F,N)
      INTEGER           N
      REAL        X(N),f(N)
      DATA        P/20./

C

C     REAL        EXP,SIN
C     INTRINSIC   EXP,SIN
C

            F(1)=2.*X(2)+X(3)+X(4)-X(6)/X(7)
            F(2)=4.*X(1)+2.*X(3)+2.*X(5)-4./X(7)
            F(3)=X(1)+X(2)+X(4)-1./X(7)
            F(5)=X(1)+X(2)+X(3)+X(4)+X(5)-1.
            F(6)=-28837.*X(1)-139009.*x(2)-78213.*x(3)+18927.
     &  X(4)+8427.*X(5)+13492./X(7)-10690*ER/X(7)
            F(7)=P*P*X(1)*X(4)**3. - 1.7837E55*X(3)*X(5)
            F(8)=X(1)*X(3)-2.6058*X(2)*X(4)
      RETURN
      END
```

VITAE

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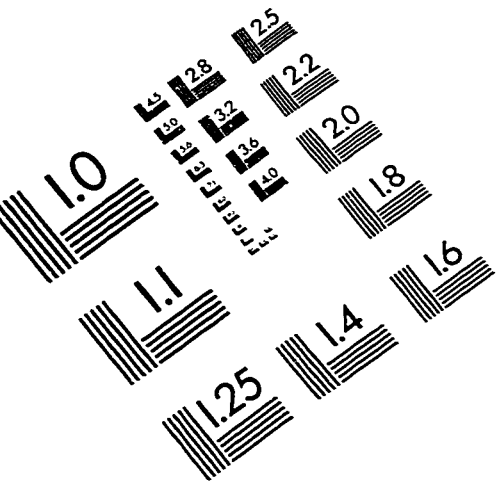
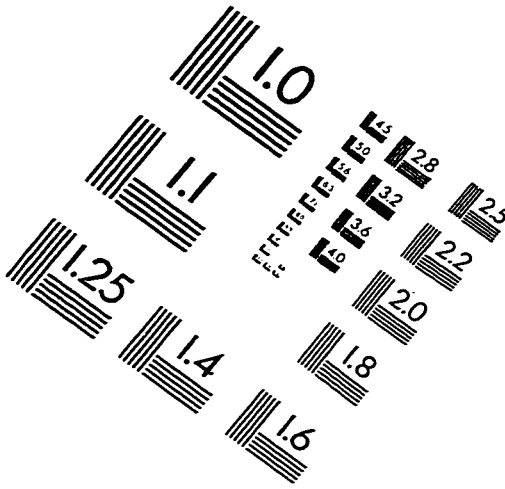
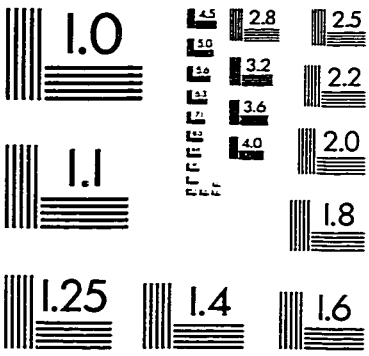
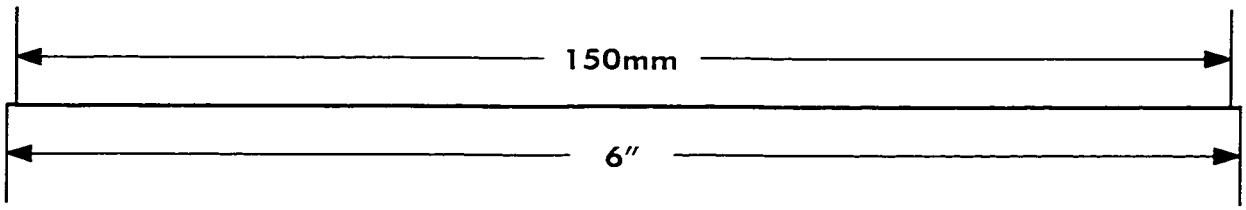
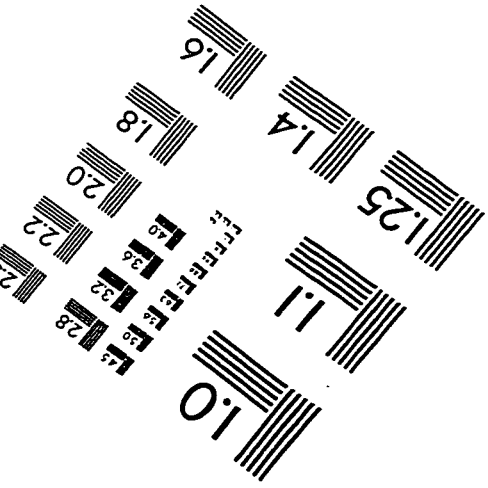
IMAGE EVALUATION TEST TARGET (QA-3)

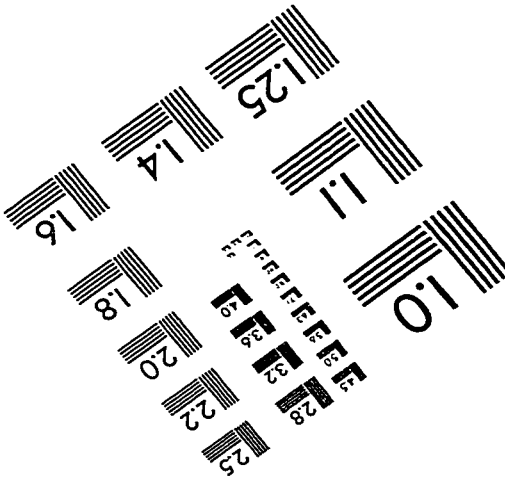












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